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最終頁に続く

(54)【発明の名称】　リチウム二次電池用正極活物質及びその製造方法、この正極活物質を用いたリチウム二次電池用正極及びその製造方法、この正極を用いたリチウム二次電池及びその製造方法

(57)【要約】
【課題】　リチウムーニッケル複合酸化物の結晶構造が強化された正極活物質を得て、サイクル特性および負荷特性が向上したリチウム二次電池用正極およびリチウム二次電池が得られるようにする。
【解決手段】　本発明のリチウム二次電池用正極活物質は、Ｘ線源としてＣｕ－Ｋαを用いた粉末Ｘ線回折測定における２θ＝１８．７１±０．２５°の範囲に存在するピークの半値幅が０．１５°～０．２２°である組成式$Li_aMn_bM_cNi_{1-(b+c)}O_2$（但し、ＭはＢ，Ａｌ，Ｆｅ，Ｖ，Ｃｒ，Ｃｕ，Ｇａ，Ｃａ，Ｍｇ，Ｓｒ，Ｔｉから選択される１種の元素であり、０＜ａ＜１．２、０．０５≦ｂ≦０．４５、０≦ｃ≦０．４５かつ０．５≦１－（ｂ＋ｃ）≦０．９５）で表されるリチウムーニッケルーマンガン複合酸化物あるいはリチウムーニッケルーマンガンーＭ複合酸化物を備えるようにしている。

【特許請求の範囲】

【請求項1】　リチウムを電気化学的に吸蔵・放出することが可能な物質を正極活物質とするリチウム二次電池用正極活物質であって、
X線源としてＣｕ－Ｋαを用いた粉末X線回折測定における２θ＝１８．７１±０．２５°の範囲に存在するピークの半値幅が０．１５°～０．２２°である組成式$Li_aMn_bM_cNi_{1-(b+c)}O_2$（但し、MはＢ，Ａｌ，Ｆｅ，Ｖ，Ｃｒ，Ｃｕ，Ｇａ，Ｃａ，Ｍｇ，Ｓｒ，Ｔｉから選択される１種の元素であり、０＜ａ＜１．２、０．０５≦ｂ≦０．４５、０≦ｃ≦０．４５かつ０．５≦１－（ｂ＋ｃ）≦０．９５）で表されるリチウム－ニッケル－マンガン複合酸化物あるいはリチウム－ニッケル－マンガン－M複合酸化物を備えたことを特徴とするリチウム二次電池用正極活物質。

【請求項2】　リチウムを電気化学的に吸蔵・放出することが可能な物質を正極活物質とするリチウム二次電池用正極活物質であって、
X線源としてＣｕ－Ｋαを用いた粉末X線回折測定における２θ＝１８．７１±０．２５°の範囲に存在するピークの半値幅が０．１５°～０．２２°である組成式$Li_aMn_bM_cNi_{1-(b+c)}O_2$（但し、MはＢ，Ａｌ，Ｆｅ，Ｖ，Ｃｒ，Ｃｕ，Ｇａ，Ｃａ，Ｍｇ，Ｓｒ，Ｔｉから選択される１種の元素であり、０＜ａ＜１．２、０．０５≦ｂ≦０．４５、０．０５≦ｃ≦０．４０かつ０．５≦１－（ｂ＋ｃ）≦０．９５）で表されるリチウム－ニッケル－マンガン－M複合酸化物を備えたことを特徴とするリチウム二次電池用正極活物質。

【請求項3】　前記組成式中のMをＡｌとしたことを特徴とする請求項１または請求項２に記載のリチウム二次電池用正極活物質。

【請求項4】　前記粉末X線回折測定において、２θ＝１８．７１±０．２５°の範囲に存在するピークの強度をI_1とし、２θ＝４４．５４±０．２５°の範囲に存在するピークの強度をI_2とした場合の強度比I_1/I_2の値が０．８以上の前記リチウム－ニッケル－マンガン複合酸化物あるいは前記リチウム－ニッケル－マンガン－M複合酸化物を選択して用いたことを特徴とする請求項１から請求項３のいずれかに記載のリチウム二次電池用正極活物質。

【請求項5】　リチウムを電気化学的に吸蔵・放出することが可能な物質を正極活物質とするリチウム二次電池用正極活物質の製造方法であって、
リチウム－ニッケル複合酸化物のニッケル原子の一部をＭｎと均一に置換するか、あるいはニッケル原子の一部をＭｎおよびM（但し、MはＢ，Ａｌ，Ｆｅ，Ｖ，Ｃｒ，Ｃｕ，Ｇａ，Ｃａ，Ｍｇ，Ｓｒ，Ｔｉから選択される１種の元素）と均一に置換する置換工程を備え、
X線源としてＣｕ－Ｋαを用いた粉末X線回折測定における２θ＝１８．７１±０．２５°の範囲に存在するピークの半値幅が０．１５°～０．２２°となる組成式$Li_aMn_bM_cNi_{1-(b+c)}O_2$（但し、Mは前記元素、０＜ａ＜１．２、０．０５≦ｂ≦０．４５、０≦ｃ≦０．４５かつ０．５≦１－（ｂ＋ｃ）≦０．９５）で表されるリチウム－ニッケル－マンガン複合酸化物あるいはリチウム－ニッケル－マンガン－M複合酸化物を形成するようにしたことを特徴とするリチウム二次電池用正極活物質の製造方法。

【請求項6】　リチウムを電気化学的に吸蔵・放出することが可能な物質を正極活物質とするリチウム二次電池用正極活物質の製造方法であって、
リチウム－ニッケル複合酸化物のニッケル原子の一部をＭｎおよびM（但し、MはＢ，Ａｌ，Ｆｅ，Ｖ，Ｃｒ，Ｃｕ，Ｇａ，Ｃａ，Ｍｇ，Ｓｒ，Ｔｉから選択される１種の元素）と均一に置換する置換工程を備え、
X線源としてＣｕ－Ｋαを用いた粉末X線回折測定における２θ＝１８．７１±０．２５°の範囲に存在するピークの半値幅が０．１５°～０．２２°となる組成式$Li_aMn_bM_cNi_{1-(b+c)}O_2$（但し、Mは前記元素、０＜ａ＜１．２、０．０５≦ｂ≦０．４５、０．０５≦ｃ≦０．４０かつ０．５≦１－（ｂ＋ｃ）≦０．９５）で表されるリチウム－ニッケル－マンガン－M複合酸化物を形成するようにしたことを特徴とするリチウム二次電池用正極活物質の製造方法。

【請求項7】　前記置換工程において、
ニッケル化合物を溶解させた水溶液とマンガン化合物を溶解させた水溶液との混合水溶液、あるいはニッケル化合物を溶解させた水溶液とマンガン化合物を溶解させた水溶液とM化合物（但し、MはＢ，Ａｌ，Ｆｅ，Ｖ，Ｃｒ，Ｃｕ，Ｇａ，Ｃａ，Ｍｇ，Ｓｒ，Ｔｉから選択される１種の元素）を溶解させた水溶液との混合水溶液のｐＨを変化させて複合水酸化物を沈殿させる共沈工程を備えるようにしたことを特徴とする請求項５または請求項６に記載のリチウム二次電池用正極活物質の製造方法。

【請求項8】　前記置換工程において、
ニッケル化合物を溶解させた水溶液とマンガン化合物を溶解させた水溶液との混合水溶液、あるいはニッケル化合物を溶解させた水溶液とマンガン化合物を溶解させた水溶液とM化合物（但し、MはＢ，Ａｌ，Ｆｅ，Ｖ，Ｃｒ，Ｃｕ，Ｇａ，Ｃａ，Ｍｇ，Ｓｒ，Ｔｉから選択される１種の元素）を溶解させた水溶液との混合水溶液を蒸発乾燥させて前記各化合物の極微粒子からなる複合原料を得る蒸発乾燥工程を備えるようにしたことを特徴とする請求項５または請求項６に記載のリチウム二次電池用正極活物質の製造方法。

【請求項9】　前記共沈工程の後、または前記蒸発乾燥工程の後、
前記共沈された複合水酸化物または前記乾燥された極微粒子からなる複合原料と、リチウム化合物との混合物を酸素雰囲気中で熱処理して複合酸化物とする熱処理工程

前記複合酸化物を粉砕して粉末とする粉砕工程とを備えるようにしたことを特徴とする請求項７または請求項８に記載のリチウム二次電池用正極活物質の製造方法。

【請求項１０】　前記組成式中のＭをＡｌとしたことを特徴とする請求項５から請求項９のいずれかに記載のリチウム二次電池用正極活物質の製造方法。

【請求項１１】　前記粉末Ｘ線回折測定において、２θ＝１８．７１±０．２５°の範囲に存在するピークの強度をI_1とし、２θ＝４４．５４±０．２５°の範囲に存在するピークの強度をI_2とした場合の強度比I_1/I_2の値が０．８以上の前記リチウムーニッケルーマンガン複合酸化物あるいは前記リチウムーニッケルーマンガンーM複合酸化物を形成するようにしたことを特徴とする請求項５から請求項１０のいずれかに記載のリチウム二次電池用正極活物質の製造方法。

【請求項１２】　少なくともリチウムを電気化学的に吸蔵・放出することが可能な正極活物質と炭素材料と結着剤とを有するリチウム二次電池用正極であって、Ｘ線源としてＣｕ－Ｋαを用いた粉末Ｘ線回折測定における２θ＝１８．７１±０．２５°の範囲に存在するピークの半値幅が０．１５°～０．２２°である組成式$Li_aMn_bM_cNi_{1-(b+c)}O_2$（但し、MはＢ，Ａｌ，Ｆｅ，Ｖ，Ｃｒ，Ｃｕ，Ｇａ，Ｃａ，Ｍｇ，Ｓｒ，Ｔｉから選択される１種の元素であり、０＜ａ＜１．２、０．０５≦ｂ≦０．４５、０≦ｃ≦０．４５かつ０．５≦１－（ｂ＋ｃ）≦０．９５）で表されるリチウムーニッケルーマンガン複合酸化物あるいはリチウムーニッケルーマンガンーM複合酸化物を前記正極活物質とし、
この正極活物質に少なくとも炭素材料と結着剤とを混合して備えたことを特徴とするリチウム二次電池用正極。

【請求項１３】　少なくともリチウムを電気化学的に吸蔵・放出することが可能な正極活物質と炭素材料と結着剤とを有するリチウム二次電池用正極であって、
Ｘ線源としてＣｕ－Ｋαを用いた粉末Ｘ線回折測定における２θ＝１８．７１±０．２５°の範囲に存在するピークの半値幅が０．１５°～０．２２°である組成式$Li_aMn_bM_cNi_{1-(b+c)}O_2$（但し、MはＢ，Ａｌ，Ｆｅ，Ｖ，Ｃｒ，Ｃｕ，Ｇａ，Ｃａ，Ｍｇ，Ｓｒ，Ｔｉから選択される１種の元素であり、０＜ａ＜１．２、０．０５≦ｂ≦０．４５、０．０５≦ｃ≦０．４０かつ０．５≦１－（ｂ＋ｃ）≦０．９５）で表されるリチウムーニッケルーマンガンーM複合酸化物を前記正極活物質とし、
この正極活物質に少なくとも炭素材料と結着剤とを混合して備えたことを特徴とするリチウム二次電池用正極。

【請求項１４】　前記組成式中のＭをＡｌとしたことを特徴とする請求項１２または請求項１３に記載のリチウム二次電池用正極。

【請求項１５】　前記粉末Ｘ線回折測定において、２θ＝１８．７１±０．２５°の範囲に存在するピークの強度をI_1とし、２θ＝４４．５４±０．２５°の範囲に存在するピークの強度をI_2とした場合の強度比I_1/I_2の値が０．８以上の前記リチウムーニッケルーマンガン複合酸化物あるいは前記リチウムーニッケルーマンガンーM複合酸化物を選択して用いるようにしたことを特徴とする請求項１２から請求項１４のいずれかに記載のリチウム二次電池用正極。

【請求項１６】　少なくともリチウムを電気化学的に吸蔵・放出することが可能な正極活物質と炭素材料と結着剤とからなるスラリーを集電体に塗着して形成するリチウム二次電池用正極の製造方法であって、
リチウムーニッケル複合酸化物のニッケル原子の一部をＭｎと均一に置換するか、あるいはニッケル原子の一部をＭｎおよびM（但し、MはＢ，Ａｌ，Ｆｅ，Ｖ，Ｃｒ，Ｃｕ，Ｇａ，Ｃａ，Ｍｇ，Ｓｒ，Ｔｉから選択される１種の元素）と均一に置換する置換工程を備え、
前記置換工程により、Ｘ線源としてＣｕ－Ｋαを用いた粉末Ｘ線回折測定における２θ＝１８．７１±０．２５°の範囲に存在するピークの半値幅が０．１５°～０．２２°となる組成式$Li_aMn_bM_cNi_{1-(b+c)}O_2$（但し、Mは前記元素、０＜ａ＜１．２、０．０５≦ｂ≦０．４５、０≦ｃ≦０．４５かつ０．５≦１－（ｂ＋ｃ）≦０．９５）で表されるリチウムーニッケルーマンガン複合酸化物あるいはリチウムーニッケルーマンガンーM複合酸化物を形成して前記正極活物質とし、
この正極活物質に少なくとも炭素材料と結着剤とを添加混合してスラリーを形成し、このスラリーを集電体に塗着するようにしたことを特徴とするリチウム二次電池用正極の製造方法。

【請求項１７】　少なくともリチウムを電気化学的に吸蔵・放出することが可能な正極活物質と炭素材料と結着剤とからなるスラリーを集電体に塗着して形成するリチウム二次電池用正極の製造方法であって、
リチウムーニッケル複合酸化物のニッケル原子の一部をＭｎおよびM（但し、MはＢ，Ａｌ，Ｆｅ，Ｖ，Ｃｒ，Ｃｕ，Ｇａ，Ｃａ，Ｍｇ，Ｓｒ，Ｔｉから選択される１種の元素）と均一に置換する置換工程を備え、
前記置換工程により、Ｘ線源としてＣｕ－Ｋαを用いた粉末Ｘ線回折測定における２θ＝１８．７１±０．２５°の範囲に存在するピークの半値幅が０．１５°～０．２２°となる組成式$Li_aMn_bM_cNi_{1-(b+c)}O_2$（但し、Mは前記元素、０＜ａ＜１．２、０．０５≦ｂ≦０．４５、０．０５≦ｃ≦０．４０かつ０．５≦１－（ｂ＋ｃ）≦０．９５）で表されるリチウムーニッケルーマンガンーM複合酸化物を形成して前記正極活物質とし、この正極活物質に少なくとも炭素材料と結着剤とを添加混合してスラリーを形成し、このスラリーを集電体に塗着するようにしたことを特徴とするリチウム二次電池用正極の製造方法。

【請求項１８】　前記置換工程において、
ニッケル化合物を溶解させた水溶液とマンガン化合物を溶解させた水溶液との混合水溶液、あるいはニッケル化合物を溶解させた水溶液とマンガン化合物を溶解させた水溶液とM化合物（但し、MはB，Ａｌ，Ｆｅ，Ｖ，Ｃｒ，Ｃｕ，Ｇａ，Ｃａ，Ｍｇ，Ｓｒ，Ｔｉから選択される１種の元素）を溶解させた水溶液との混合水溶液のｐＨを変化させて複合水酸化物を沈殿させる共沈工程を備えるようにしたことを特徴とする請求項１７または請求項１８に記載のリチウム二次電池用正極の製造方法。

【請求項１９】　前記置換工程において、
ニッケル化合物を溶解させた水溶液とマンガン化合物を溶解させた水溶液との混合水溶液、あるいはニッケル化合物を溶解させた水溶液とマンガン化合物を溶解させた水溶液とM化合物（但し、MはB，Ａｌ，Ｆｅ，Ｖ，Ｃｒ，Ｃｕ，Ｇａ，Ｃａ，Ｍｇ，Ｓｒ，Ｔｉから選択される１種の元素）を溶解させた水溶液との混合水溶液を蒸発乾燥させて前記各化合物の極微粒子からなる複合原料を得る蒸発乾燥工程を備えるようにしたことを特徴とする請求項１７または請求項１８に記載のリチウム二次電池用正極の製造方法。

【請求項２０】　前記共沈工程の後、または前記蒸発乾燥工程の後、
前記共沈された複合水酸化物または前記乾燥された極微粒子からなる複合原料と、リチウム化合物との混合物を酸素雰囲気中で熱処理して複合酸化物とする熱処理工程と、
前記複合酸化物を粉砕して粉末とする粉砕工程とを備えるようにしたことを特徴とする請求項１８または請求項１９に記載のリチウム二次電池用正極の製造方法。

【請求項２１】　前記組成式中のMをＡｌとしたことを特徴とする請求項１６から請求項２０のいずれかに記載のリチウム二次電池用正極の製造方法。

【請求項２２】　前記X線回折測定において、２θ＝１８．７１±０．２５°の範囲に存在するピークの強度をI_1とし、２θ＝４４．５４±０．２５°の範囲に存在するピークの強度をI_2とした場合の強度比I_1/I_2の値が０．８以上の前記リチウムーニッケルーマンガン複合酸化物あるいはリチウムーニッケルーマンガンーM複合酸化物を形成して前記正極活物質としたことを特徴とする請求項１６から請求項２２のいずれかに記載のリチウム二次電池用正極の製造方法。

【請求項２３】　少なくともリチウムを電気化学的に吸蔵・放出することが可能な正極活物質と炭素材料と結着剤とを有する正極と、リチウム金属、リチウム合金またはリチウムを電気化学的に吸蔵・放出することが可能な負極と、これら両極を隔離するセパレータと、非水電解液とを備えたリチウム二次電池であって、
X線源としてＣｕ－Ｋαを用いた粉末X線回折測定における２θ＝１８．７１±０．２５°の範囲に存在するピークの半値幅が０．１５°～０．２２°である組成式$Li_aMn_bM_cNi_{1-(b+c)}O_2$（但し、MはB，Ａｌ，Ｆｅ，Ｖ，Ｃｒ，Ｃｕ，Ｇａ，Ｃａ，Ｍｇ，Ｓｒ，Ｔｉから選択される１種の元素であり、０＜ａ＜１．２、０．０５≦ｂ≦０．４５、０≦ｃ≦０．４５かつ０．５≦１－（ｂ＋ｃ）≦０．９５）で表されるリチウムーニッケルーマンガン複合酸化物あるいはリチウムーニッケルーマンガンーM複合酸化物を前記正極活物質とし、
この正極活物質に少なくとも炭素材料と結着剤とが混合された正極と、リチウム金属、リチウム合金またはリチウムを電気化学的に吸蔵・放出することが可能な負極と、これら両極を隔離するセパレータと、非水電解液とを備えたことを特徴とするリチウム二次電池。

【請求項２４】　少なくともリチウムを電気化学的に吸蔵・放出することが可能な正極活物質と炭素材料と結着剤とを有する正極と、リチウム金属またはリチウムを電気化学的に吸蔵・放出することが可能な負極と、これら両極を隔離するセパレータと、非水電解液とを備えたリチウム二次電池であって、
X線源としてＣｕ－Ｋαを用いた粉末X線回折測定における２θ＝１８．７１±０．２５°の範囲に存在するピークの半値幅が０．１５°～０．２２°である組成式$Li_aMn_bM_cNi_{1-(b+c)}O_2$（但し、MはB，Ａｌ，Ｆｅ，Ｖ，Ｃｒ，Ｃｕ，Ｇａ，Ｃａ，Ｍｇ，Ｓｒ，Ｔｉから選択される１種の元素であり、０＜ａ＜１．２、０．０５≦ｂ≦０．４５、０．０５≦ｃ≦０．４０かつ０．５≦１－（ｂ＋ｃ）≦０．９５）で表されるリチウムーニッケルーマンガンーM複合酸化物を前記正極活物質とし、
この正極活物質に少なくとも炭素材料と結着剤とが混合された正極と、リチウム金属、リチウム合金またはリチウムを電気化学的に吸蔵・放出することが可能な負極と、これら両極を隔離するセパレータと、非水電解液とを備えたことを特徴とするリチウム二次電池。

【請求項２５】　前記組成式中のMをＡｌとしたことを特徴とする請求項２３または請求項２４に記載のリチウム二次電池。

【請求項２６】　前記X線回折測定において、２θ＝１８．７１±０．２５°の範囲に存在するピークの強度をI_1とし、２θ＝４４．５４±０．２５°の範囲に存在するピークの強度をI_2とした場合の強度比I_1/I_2の値が０．８以上の前記リチウムーニッケルーマンガン複合酸化物あるいは前記リチウムーニッケルーマンガンーM複合酸化物を前記正極活物質として選択して用いたことを特徴とする請求項２３から請求項２５のいずれかに記載のリチウム二次電池。

【請求項２７】　少なくともリチウムを電気化学的に吸蔵・放出することが可能な正極活物質と炭素材料と結着剤とを有する正極と、リチウム金属、リチウム合金またはリチウムを電気化学的に吸蔵・放出することが可能な

負極と、これら両極を隔離するセパレータと、非水電解液とを備えたリチウム二次電池の製造方法であって、
リチウム－ニッケル複合酸化物のニッケル原子の一部をＭｎと均一に置換するか、あるいはニッケル原子の一部をＭｎおよびＭ（但し、ＭはＢ，Ａｌ，Ｆｅ，Ｖ，Ｃｒ，Ｃｕ，Ｇａ，Ｃａ，Ｍｇ，Ｓｒ，Ｔｉから選択される１種の元素）と均一に置換する置換工程を備え、
前記置換工程により、Ｘ線源としてＣｕ－Ｋαを用いた粉末Ｘ線回折測定における２θ＝１８．７１±０．２５°の範囲に存在するピークの半値幅が０．１５°～０．２２°となる組成式$Li_aMn_bM_cNi_{1-(b+c)}O_2$（但し、Ｍは前記元素、０＜ａ＜１．２、０．０５≦ｂ≦０．４５、０≦ｃ≦０．４５かつ０．５≦１－（ｂ＋ｃ）≦０．９５）で表されるリチウム－ニッケル－マンガン複合酸化物あるいはリチウム－ニッケル－マンガン－Ｍ複合酸化物を形成して前記正極活物質とし、
この正極活物質に少なくとも炭素材料と結着剤とを添加混合してスラリーを形成し、このスラリーを集電体に塗着して前記正極を形成する正極形成工程と、
前記正極形成工程により形成された正極を前記セパレータを介在させて前記リチウム金属、リチウム合金またはリチウムを電気化学的に吸蔵・放出することが可能な負極とを重ね合わせて電池缶に挿入した後、この電池缶内に非水電解液を充填して形成することを特徴とするリチウム二次電池の製造方法。

【請求項２８】　少なくともリチウムを電気化学的に吸蔵・放出することが可能な正極活物質と炭素材料と結着剤とを有する正極と、リチウム金属、リチウム合金またはリチウムを電気化学的に吸蔵・放出することが可能な負極と、これら両極を隔離するセパレータと、非水電解液とを備えたリチウム二次電池の製造方法であって、
リチウム－ニッケル複合酸化物のニッケル原子の一部をＭｎおよびＭ（但し、ＭはＢ，Ａｌ，Ｆｅ，Ｖ，Ｃｒ，Ｃｕ，Ｇａ，Ｃａ，Ｍｇ，Ｓｒ，Ｔｉから選択される１種の元素）と均一に置換する置換工程を備え、
前記置換工程により、Ｘ線源としてＣｕ－Ｋαを用いた粉末Ｘ線回折測定における２θ＝１８．７１±０．２５°の範囲に存在するピークの半値幅が０．１５°～０．２２°となる組成式$Li_aMn_bM_cNi_{1-(b+c)}O_2$（但し、Ｍは前記元素、０＜ａ＜１．２、０．０５≦ｂ≦０．４５、０．０５≦ｃ≦０．４０かつ０．５≦１－（ｂ＋ｃ）≦０．９５）で表されるリチウム－ニッケル－マンガン－Ｍ複合酸化物を形成して前記正極活物質とし、
この正極活物質に少なくとも炭素材料と結着剤とを添加混合してスラリーを形成し、このスラリーを集電体に塗着して前記正極を形成する正極形成工程と、
前記正極形成工程により形成された正極を前記セパレータを介在させて前記リチウム金属、リチウム合金またはリチウムを電気化学的に吸蔵・放出することが可能な負極とを重ね合わせて電池缶に挿入した後、この電池缶内に非水電解液を充填して形成することを特徴とするリチウム二次電池の製造方法。

【請求項２９】　前記置換工程において、
ニッケル化合物を溶解させた水溶液とマンガン化合物を溶解させた水溶液との混合水溶液、あるいはニッケル化合物を溶解させた水溶液とマンガン化合物を溶解させた水溶液とＭ化合物（但し、ＭはＢ，Ａｌ，Ｆｅ，Ｖ，Ｃｒ，Ｃｕ，Ｇａ，Ｃａ，Ｍｇ，Ｓｒ，Ｔｉから選択される１種の元素）を溶解させた水溶液との混合水溶液のｐＨを変化させて複合水酸化物を沈殿させる共沈工程を備えるようにしたことを特徴とする請求項２７または請求項２８に記載のリチウム二次電池の製造方法。

【請求項３０】　前記置換工程において、
ニッケル化合物を溶解させた水溶液とマンガン化合物を溶解させた水溶液との混合水溶液、あるいはニッケル化合物を溶解させた水溶液とマンガン化合物を溶解させた水溶液とＭ化合物（但し、ＭはＢ，Ａｌ，Ｆｅ，Ｖ，Ｃｒ，Ｃｕ，Ｇａ，Ｃａ，Ｍｇ，Ｓｒ，Ｔｉから選択される１種の元素）を溶解させた水溶液との混合水溶液を蒸発乾燥させて前記各化合物の極微粒子からなる複合原料を得る蒸発乾燥工程を備えるようにしたことを特徴とする請求項２７または請求項２８に記載のリチウム二次電池の製造方法。

【請求項３１】　前記共沈工程の後、または前記蒸発乾燥工程の後、
前記共沈された複合水酸化物または前記乾燥された極微粒子からなる複合原料と、リチウム化合物との混合物を酸素雰囲気中で熱処理して複合酸化物とする熱処理工程と、
前記複合酸化物を粉砕して粉末とする粉砕工程とを備えるようにしたことを特徴とする請求項２７から請求項３０のいずれかに記載のリチウム二次電池の製造方法。

【請求項３２】　前記組成式中のＭをＡｌとしたことを特徴とする請求項２７から請求項３１のいずれかに記載のリチウム二次電池の製造方法。

【請求項３３】　前記Ｘ線回折測定において、２θ＝１８．７１±０．２５°の範囲に存在するピークの強度をI_1とし、２θ＝４４．５４±０．２５°の範囲に存在するピークの強度をI_2とした場合の強度比I_1/I_2の値が０．８以上の前記リチウム－ニッケル－マンガン複合酸化物あるいは前記リチウム－ニッケル－マンガン－Ｍ複合酸化物を形成するようにしたことを特徴とする請求項２７から請求項３２のいずれかに記載のリチウム二次電池の製造方法。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明はリチウムを電気化学的に吸蔵・放出することが可能な正極活物質に係り、特にサイクル特性および負荷特性が向上したリチウム二次

電池用正極活物質およびその製造方法、この正極活物質を用いたリチウム二次電池用正極及びその製造方法、この正極を用いたリチウム二次電池及びその製造方法の改良に関する。

【０００２】

【従来の技術】近年、小型ビデオカメラ、携帯電話、ノートパソコン等の携帯用電子・通信機器等に用いられる電池として、金属リチウム、リチウム合金あるいはリチウムイオンを吸蔵・放出できる炭素材料などを負極活物質とし、リチウム－コバルト複合酸化物（$LiCoO_2$）、リチウム－ニッケル複合酸化物（$LiNiO_2$）、リチウム－マンガン複合酸化物（$LiMn_2O_4$）等のリチウム含有遷移金属複合酸化物を正極材料とするリチウムイオン電池で代表されるリチウム二次電池が、４Ｖ級の高い放電電圧が得られるとともに、エネルギー密度が高く、小型軽量でかつ高容量で充放電可能な電池として注目されるようになり、これらのうちリチウム－コバルト複合酸化物（$LiCoO_2$）を正極材料とするリチウム二次電池が実用化されるようになった。

【０００３】しかしながら、リチウム－ニッケル複合酸化物（$LiNiO_2$）を正極材料とするリチウム二次電池は実用化に至っていない。この原因の１つとして、リチウム－ニッケル複合酸化物（$LiNiO_2$）はリチウムイオンの吸蔵・放出に伴い、結晶構造に乱れを生じ易く、その結果、良好なサイクル特性が得られないことが挙げられる。また、結晶構造が脆いため、高率での充放電によるリチウムイオンの急激な吸蔵・放出に耐えられないことが挙げられる。

【０００４】そこで、リチウム－ニッケル複合酸化物（$LiNiO_2$）のニッケル元素の一部を他の元素で置換し、結晶構造を強化してサイクル特性を向上させる検討が行われるようになった。例えば、特開平８－３７００７号公報においては、リチウム－ニッケル複合酸化物（$LiNiO_2$）のニッケル元素の一部をコバルト元素およびマンガン元素で置換させることにより、結晶構造を安定化させ、さらに＋３価のマンガンを含むマンガン化合物を用いることにより、電気化学的に不活性なLi_2MnO_3や岩塩構造のNiOの生成を抑制することが提案されている。

【０００５】

【発明が解決しようとする課題】しかしながら、特開平８－３７００７号公報において提案された方法であっても十分ではなかった。これは、この公報において提案された方法でリチウム化合物とニッケル化合物とコバルト化合物とマンガン化合物とを熱処理した場合には、ニッケル元素の一部をコバルト元素およびマンガン元素で置換して複合化をさせていない場合と比較してサイクル特性は向上するが、まだ不十分であった。

【０００６】これは、置換されたコバルト元素およびマンガン元素の分布が不均一であり、結晶構造を強化する効果が十分に発揮されていないためと考えられる。一般に、ある物質に異種元素が不均一に固溶した場合、粉末Ｘ線回折におけるピークの半値幅が増加することが知られているが、上述した特開平８－３７００７号公報において提案された方法により得られたリチウム－ニッケル－コバルト－マンガン複合酸化物の粉末Ｘ線回折におけるピークの半値幅が、ニッケル以外の元素を固溶させない場合の半値幅よりも大きくなっていることからも、コバルト元素およびマンガン元素の固溶が不均一であることを示唆しているということができる。

【０００７】

【課題を解決するための手段およびその作用・効果】そこで、本発明は上記した課題を解決するためになされたものであって、リチウム－ニッケル複合酸化物の結晶構造が強化された正極活物質を得て、サイクル特性および負荷特性が向上したリチウム二次電池用正極およびリチウム二次電池が得られるようにすることを目的とするものである。

【０００８】このため、本発明のリチウム二次電池用正極活物質は、Ｘ線源としてＣｕ－Ｋαを用いた粉末Ｘ線回折測定における$2\theta=18.71\pm0.25°$の範囲に存在するピークの半値幅が$0.15°\sim0.22°$である組成式$Li_aMn_bM_cNi_{1-(b+c)}O_2$（但し、ＭはＢ，Ａｌ，Ｆｅ，Ｖ，Ｃｒ，Ｃｕ，Ｇａ，Ｃａ，Ｍｇ，Ｓｒ，Ｔｉから選択される１種の元素であり、$0<a<1.2$、$0.05\leqq b\leqq0.45$、$0\leqq c\leqq0.45$かつ$0.5\leqq1-(b+c)\leqq0.95$）で表されるリチウム－ニッケル－マンガン複合酸化物あるいはリチウム－ニッケル－マンガン－Ｍ複合酸化物を備えるようにしている。

【０００９】また、本発明のリチウム二次電池用正極活物質は、Ｘ線源としてＣｕ－Ｋαを用いた粉末Ｘ線回折測定における$2\theta=18.71\pm0.25°$の範囲に存在するピークの半値幅が$0.15°\sim0.22°$である組成式$Li_aMn_bM_cNi_{1-(b+c)}O_2$（但し、ＭはＢ，Ａｌ，Ｆｅ，Ｖ，Ｃｒ，Ｃｕ，Ｇａ，Ｃａ，Ｍｇ，Ｓｒ，Ｔｉから選択される１種の元素であり、$0<a<1.2$、$0.05\leqq b\leqq0.45$、$0.05\leqq c\leqq0.40$かつ$0.5\leqq1-(b+c)\leqq0.95$）で表されるリチウム－ニッケル－マンガン－Ｍ複合酸化物を備えるようにしている。

【００１０】$LiNiO_2$で表されるリチウム－ニッケル複合酸化物は、リチウムイオンの吸蔵・放出に伴い結晶構造が壊れて放電容量が低下するが、これは結晶構造が脆いことに原因があると考えられる。しかしながら、リチウム－ニッケル複合酸化物（$LiNiO_2$）のニッケル元素の一部をＭｎあるいはＭｎとＭ（ＭはＢ，Ａｌ，Ｆｅ，Ｖ，Ｃｒ，Ｃｕ，Ｇａ，Ｃａ，Ｍｇ，Ｓｒ，Ｔｉから選択される１種の元素）で置換された上記組成式で表されるリチウム－ニッケル－マンガン複合酸化物

あるいはリチウム−ニッケル−マンガン−M複合酸化物は、X線源としてＣｕ−Ｋαを用いた粉末X線回折測定における２θ＝１８．７１±０．２５°の範囲に存在するピークの半値幅が０．１５°〜０．２２°であると、ニッケル元素の一部がＭｎあるいはＭｎと他の元素Mと均一に置換されているので、結晶構造が強化される。

【００１１】リチウム−ニッケル複合酸化物（$LiNiO_2$）のX線源としてＣｕ−Ｋαを用いた粉末X線回折測定における２θ＝１８．７１±０．２５°の範囲に存在するピークの半値幅が０．１５°〜０．２２°であることは、結晶構造に乱れを生じさせることなく、均一に異種元素で置換できていることを示唆している。リチウム−ニッケル複合酸化物（$LiNiO_2$）のニッケル元素の一部がＭｎあるいはＭｎと他の元素Mと均一に置換されたリチウム−ニッケル−マンガン複合酸化物あるいはリチウム−ニッケル−マンガン−M複合酸化物は、結晶構造が強化されるため、サイクル特性および負荷特性が向上した正極活物質となる。したがって、この活物質を用いた正極のサイクル特性および負荷特性が向上するとともに、この正極を用いたリチウム二次電池のサイクル特性および負荷特性が向上する。

【００１２】そして、このような複合酸化物としてリチウム−ニッケル−マンガン−アルミニウム複合酸化物を用いると、サイクル特性および負荷特性が特に向上した正極活物質となる。したがって、このような複合酸化物からなる活物質を用いた正極のサイクル特性および負荷特性が特に向上するとともに、この正極を用いたリチウム二次電池のサイクル特性および負荷特性が特に向上する。

【００１３】また、リチウム−ニッケル複合酸化物（$LiNiO_2$）のニッケル元素の一部がＭｎあるいはＭｎと他の元素Mと均一に置換されたリチウム−ニッケル−マンガン複合酸化物あるいはリチウム−ニッケル−マンガン−M複合酸化物を用いた場合、粉末X線回折測定において、２θ＝１８．７１±０．２５°の範囲に存在するピークの強度をI_1とし、２θ＝４４．５４±０．２５°の範囲に存在するピークの強度をI_2とした場合の強度比I_1/I_2の値が０．８を下回ると、$Li_2Ni_8O_{10}$などの不純物の生成が考えられ、これらの不純物は結晶構造に悪影響を及ぼし、容量低下などを招くため、強度比I_1/I_2の値は０．８以上にすることが望ましい。

【００１４】そして、リチウム−ニッケル複合酸化物（$LiNiO_2$）のニッケル元素の一部がＭｎあるいはＭｎと他の元素Mと均一に置換されたリチウム−ニッケル−マンガン複合酸化物あるいはリチウム−ニッケル−マンガン−M複合酸化物を製造する場合、従来から行われているような原料粉末を混合して焼成する等の合成法では、リチウム−ニッケル複合酸化物（$LiNiO_2$）のニッケル元素の一部を、ＭｎあるいはＭｎと他の元素Mと均一に置換することは難しく、その結果、粉末X線回折測定におけるピークの半値幅が大きくなり、置換によるサイクル特性の向上および負荷特性の向上が不十分となった。

【００１５】そこで、本発明の正極活物質の製造方法においては、リチウム−ニッケル複合酸化物（$LiNiO_2$）のニッケル元素の一部をＭｎあるいはＭｎと他の元素Mで均一に置換する方策が必要となる。例えば、ニッケル化合物を溶解させた水溶液とマンガン化合物を溶解させた水溶液との混合水溶液、あるいはニッケル化合物を溶解させた水溶液とマンガン化合物を溶解させた水溶液とM化合物（但し、MはＢ，Ａｌ，Ｆｅ，Ｖ，Ｃｒ，Ｃｕ，Ｇａ，Ｃａ，Ｍｇ，Ｓｒ，Ｔｉから選択される１種の元素）を溶解させた水溶液との混合水溶液のｐＨを変化させて複合水酸化物を沈殿させる共沈工程を備えることが挙げられる。

【００１６】また、他の例としては、ニッケル化合物を溶解させた水溶液とマンガン化合物を溶解させた水溶液との混合水溶液、あるいはニッケル化合物を溶解させた水溶液とマンガン化合物を溶解させた水溶液とM化合物（但し、MはＢ，Ａｌ，Ｆｅ，Ｖ，Ｃｒ，Ｃｕ，Ｇａ，Ｃａ，Ｍｇ，Ｓｒ，Ｔｉから選択される１種の元素）を溶解させた水溶液との混合水溶液を蒸発乾燥させて各化合物の極微粒子からなる複合原料を得る蒸発乾燥工程を備えることが挙げられる。そして、これらの工程（共沈工程または蒸発乾燥工程）によって得られた複合水酸化物または極微粒子からなる複合原料と、リチウム化合物との混合物を酸素雰囲気中で熱処理することにより、リチウム−ニッケル複合酸化物（$LiNiO_2$）のニッケル元素の一部がＭｎあるいはＭｎと他の元素Mで均一に置換されたリチウム−ニッケル−マンガン複合酸化物あるいはリチウム−ニッケル−マンガンM複合酸化物が得られる。

【００１７】これらの共沈工程あるいは蒸発乾燥工程を備えるようにすると、リチウム−ニッケル複合酸化物（$LiNiO_2$）のニッケル元素の一部がＭｎあるいはＭｎと他の元素M（但し、MはＢ，Ａｌ，Ｆｅ，Ｖ，Ｃｒ，Ｃｕ，Ｇａ，Ｃａ，Ｍｇ，Ｓｒ，Ｔｉから選択される１種の元素）と極めて均一に置換されたリチウム−ニッケル−マンガン複合酸化物あるいはリチウム−ニッケル−マンガン−M複合酸化物が得られるようになる。このようなリチウム−ニッケル−マンガン複合酸化物あるいはリチウム−ニッケル−マンガン−M複合酸化物は結晶構造が十分に強化され、サイクル特性および負荷特性が特に向上した正極活物質となる。したがって、このような複合酸化物からなる活物質を用いた正極のサイクル特性および負荷特性が特に向上するとともに、この正極を用いたリチウム二次電池のサイクル特性および負荷特性が特に向上する。

【００１８】

【発明の実施の形態】ついで、本発明の実施形態を以下

に説明する。

1．正極活物質の作製

（1）実施例１～３

まず、硫酸ニッケル水溶液のニッケルのモル比と、硫酸マンガン水溶液のマンガンのモル比を９５：５、７０：３０および５５：４５に調製した３種類の混合水溶液を用意する。ついで、これらの混合水溶液を撹拌槽内に充填した後、この撹拌槽を回転させて撹拌しながら、混合水溶液に水酸化ナトリウム水溶液を徐々に添加して、混合水溶液のｐＨを調製した。この撹拌により、水酸化ニッケルのニッケル元素の一部をマンガン元素により置換された構造を有する、組成式$Ni_{0.95}Mn_{0.05}(OH)_2$、$Ni_{0.70}Mn_{0.30}(OH)_2$および$Ni_{0.55}Mn_{0.45}(OH)_2$で示される３種類のニッケル－マンガン複合水酸化物をそれぞれ得た。

【００１９】ついで、これらのニッケル－マンガン複合水酸化物と水酸化リチウム（ＬｉＯＨ）とを、リチウムとニッケル－マンガンとのモル比がそれぞれ１：１となるようにそれぞれ調製して混合した後、７５０℃の酸素雰囲気で２０時間熱処理して、粒状塊を得た。この後、この粒状塊を粉砕して、組成式$LiNi_{0.95}Mn_{0.05}O_2$（実施例1）、$LiNi_{0.70}Mn_{0.30}O_2$（実施例2）および$LiNi_{0.55}Mn_{0.45}O_2$（実施例3）で示される３種類のリチウム－ニッケル－マンガン複合酸化物からなる正極活物質をそれぞれ得た。

【００２０】（2）実施例4～6

まず、硫酸ニッケル水溶液のニッケルのモル比と、硫酸マンガン水溶液のマンガンのモル比と、硫酸アルミニウム水溶液のアルミニウムのモル比を９０：５：５、６５：３０：５および５０：４５：５に調製した３種類の混合水溶液を用意する。ついで、これらの混合水溶液を上述した実施例１～３と同様にして撹拌して、水酸化ニッケルのニッケル元素の一部をマンガン元素およびアルミニウムにより置換された構造を有する、組成式$Ni_{0.90}Mn_{0.05}Al_{0.05}(OH)_2$、$Ni_{0.65}Mn_{0.30}Al_{0.05}(OH)_2$および$Ni_{0.50}Mn_{0.45}Al_{0.05}(OH)_2$で示される３種類のニッケル－マンガン－アルミニウム複合水酸化物をそれぞれ得た。

【００２１】ついで、リチウムとニッケル－マンガン－アルミニウムとのモル比がそれぞれ１：１となるようにそれぞれ調製して混合した後、上述した実施例１～３と同様にして熱処理および粉砕して、組成式$LiNi_{0.90}Mn_{0.05}Al_{0.05}O_2$（実施例4）、$LiNi_{0.65}Mn_{0.30}Al_{0.05}O_2$（実施例5）および$LiNi_{0.50}Mn_{0.45}Al_{0.05}O_2$（実施例6）で示される３種類のリチウム－ニッケル－マンガン－アルミニウム複合酸化物からなる正極活物質をそれぞれ得た。

【００２２】（3）実施例7～9

まず、硫酸ニッケル水溶液のニッケルのモル比と、硫酸マンガン水溶液のマンガンのモル比と、硫酸アルミニウム水溶液のアルミニウムのモル比を８５：５：１０、７０：２０：１０および５０：４０：１０に調製した３種類の混合水溶液を用意する。ついで、これらの混合水溶液を上述した実施例１～３と同様にして撹拌して、水酸化ニッケルのニッケル元素の一部をマンガン元素およびアルミニウムにより置換された構造を有する、組成式$Ni_{0.85}Mn_{0.05}Al_{0.10}(OH)_2$、$Ni_{0.70}Mn_{0.20}Al_{0.10}(OH)_2$および$Ni_{0.50}Mn_{0.40}Al_{0.10}(OH)_2$で示される３種類のニッケル－マンガン－アルミニウム複合水酸化物をそれぞれ得た。

【００２３】ついで、リチウムとニッケル－マンガン－アルミニウムとのモル比がそれぞれ１：１となるようにそれぞれ調製して混合した後、上述した実施例１～３と同様にして熱処理および粉砕して、組成式$LiNi_{0.85}Mn_{0.05}Al_{0.10}O_2$（実施例8）、$LiNi_{0.70}Mn_{0.20}Al_{0.10}O_2$（実施例9）および$LiNi_{0.50}Mn_{0.40}Al_{0.10}O_2$（実施例１０）で示される３種類のリチウム－ニッケル－マンガン－アルミニウム複合酸化物からなる正極活物質をそれぞれ得た。

【００２４】（4）実施例１０～１２

まず、硫酸ニッケル水溶液のニッケルのモル比と、硫酸マンガン水溶液のマンガンのモル比と、硫酸アルミニウム水溶液のアルミニウムのモル比を６５：５：３０、６０：１０：３０および５０：２０：３０に調製した３種類の混合水溶液を用意する。ついで、これらの混合水溶液を上述した実施例１～３と同様にして撹拌して、水酸化ニッケルのニッケル元素の一部をマンガン元素およびアルミニウムにより置換された構造を有する、組成式$Ni_{0.65}Mn_{0.05}Al_{0.30}(OH)_2$、$Ni_{0.60}Mn_{0.10}Al_{0.30}(OH)_2$および$Ni_{0.50}Mn_{0.20}Al_{0.30}(OH)_2$で示される３種類のニッケル－マンガン－アルミニウム複合水酸化物をそれぞれ得た。

【００２５】ついで、リチウムとニッケル－マンガン－アルミニウムとのモル比がそれぞれ１：１となるようにそれぞれ調製して混合した後、上述した実施例１～３と同様にして熱処理および粉砕して、組成式$LiNi_{0.65}Mn_{0.05}Al_{0.30}O_2$（実施例１０）、$LiNi_{0.60}Mn_{0.10}Al_{0.30}O_2$（実施例１１）および$LiNi_{0.50}Mn_{0.20}Al_{0.30}O_2$（実施例１２）で示される３種類のリチウム－ニッケル－マンガン－アルミニウム複合酸化物からなる正極活物質をそれぞれ得た。

【００２６】（5）実施例１３～１５

まず、硫酸ニッケル水溶液のニッケルのモル比と、硫酸マンガン水溶液のマンガンのモル比と、硫酸アルミニウム水溶液のアルミニウムのモル比を５５：５：４０、５０：１０：４０および５０：５：４５に調製した３種類の混合水溶液を用意する。ついで、これらの混合水溶液を上述した実施例１～３と同様にして撹拌して、水酸化ニッケルのニッケル元素の一部をマンガン元素およびアルミニウムにより置換された構造を有する、組成式Ｎｉ

$_{0.55}$Mn$_{0.05}$Al$_{0.40}$（OH）$_2$、Ni$_{0.50}$Mn$_{0.10}$Al$_{0.40}$（OH）$_2$およびNi$_{0.50}$Mn$_{0.05}$Al$_{0.45}$（OH）$_2$で示される３種類のニッケルーマンガンーアルミニウム複合水酸化物をそれぞれ得た。

【００２７】ついで、リチウムとニッケルーマンガンーアルミニウムとのモル比がそれぞれ１：１となるようにそれぞれ調製して混合した後、上述した実施例１～３と同様にして熱処理および粉砕して、組成式LiNi$_{0.55}$Mn$_{0.05}$Al$_{0.40}$O$_2$（実施例１３）、LiNi$_{0.50}$Mn$_{0.10}$Al$_{0.40}$O$_2$（実施例１４）およびLiNi$_{0.50}$Mn$_{0.05}$Al$_{0.45}$O$_2$（実施例１５）で示される３種類のリチウムーニッケルーマンガンーアルミニウム複合酸化物からなる正極活物質をそれぞれ得た。

【００２８】上述のようにして作製した実施例１～実施例１５の各正極活物質を順次粉末X線回折測定装置内に配置し、X線源としてCu－Kαとスリット幅が１μmのスリットを用いて、各正極活物質にCu－Kαを照射角θで照射して２θ＝１８．７１±０．２５°の範囲に存在するピークの半値幅を測定すると、下記の表１に示すような結果となった。また、２θ＝１８．７１±０．２５°の範囲に存在するピークの強度I$_1$を測定するとともに、２θ＝４４．５４±０．２５°の範囲に存在するピークの強度I$_2$を測定した後、ピークの強度比I$_1$／I$_2$を求めると、下記の表１に示すような結果となった。

【００２９】

【表１】

正極活物質の種類	各元素のモル比				b＋c	半値幅（°）	ピークの強度比
	Li	Ni	Mn	Al			
実施例１	1.00	0.95	0.05	0.00	0.05	0.16	1.8
実施例２	1.00	0.70	0.30	0.00	0.30	0.20	1.5
実施例３	1.00	0.55	0.45	0.00	0.45	0.22	1.7
実施例４	1.00	0.90	0.05	0.05	0.10	0.18	1.3
実施例５	1.00	0.65	0.30	0.05	0.35	0.20	1.1
実施例６	1.00	0.50	0.45	0.05	0.50	0.19	1.3
実施例７	1.00	0.85	0.05	0.10	0.15	0.17	1.5
実施例８	1.00	0.70	0.20	0.10	0.30	0.18	1.5
実施例９	1.00	0.50	0.40	0.10	0.50	0.20	1.9
実施例10	1.00	0.65	0.05	0.30	0.35	0.20	1.7
実施例11	1.00	0.60	0.10	0.30	0.40	0.17	1.8
実施例12	1.00	0.50	0.20	0.30	0.50	0.18	1.5
実施例13	1.00	0.55	0.05	0.40	0.45	0.22	1.7
実施例14	1.00	0.50	0.10	0.40	0.50	0.21	1.1
実施例15	1.00	0.50	0.05	0.45	0.50	0.21	1.2

【００３０】なお、上記表１において、各元素のモル比においてLiは組成式Li$_a$Mn$_b$M$_c$Ni$_{1-(b+c)}$O$_2$におけるaを表し、Niは１－（b＋c）を表し、Mnはbを表し、Al（MがAlの場合）はcを表している。上記表１より明らかなように、X線源としてCu－Kαを用いた粉末X線回折測定における２θ＝１８．７１±０．２５°の範囲に存在するピークの半値幅が０．１５°～０．２２°である各実施例１～１５の複合酸化物は、０＜a＜１．２、０．０５≦b≦０．４５、０≦c≦０．４５かつ、０．０５≦b＋c≦０．５０、即ち、０．５≦１－（b＋c）≦０．９５の条件のいづれをも満たしていることが分かる。

【００３１】（６）比較例１

まず、硫酸ニッケル水溶液を撹拌槽内に充填した後、この撹拌槽を回転させて撹拌しながら、この水溶液に水酸化ナトリウム水溶液を徐々に添加して、水溶液のpHを調製した。この撹拌により、水酸化ニッケルを得た。ついで、水酸化ニッケルと水酸化リチウムとを、リチウムとニッケルとのモル比がそれぞれ１：１となるようにそれぞれ調製して混合した後、７５０℃の酸素雰囲気で２０時間熱処理して、粒状塊を得た。この後、この粒状塊を粉砕して、組成式LiNiO$_2$（比較例１）で示されるリチウムーニッケル複合酸化物からなる正極活物質を得た。

【００３２】（７）比較例２

まず、硫酸ニッケル水溶液のニッケルのモル比と、硫酸マンガン水溶液のマンガンのモル比を５０：５０に調製した混合水溶液を用意する。ついで、この混合水溶液を撹拌槽内に充填した後、この撹拌槽を回転させて撹拌しながら、混合水溶液に水酸化ナトリウム水溶液を徐々に添加して、混合水溶液のpHを調製した。この撹拌により、水酸化ニッケルのニッケル元素の一部をマンガン元

素により置換された構造を有する、組成式$Ni_{0.50}Mn_{0.50}(OH)_2$で示されるニッケル－マンガン複合水酸化物を得た。

【００３３】ついで、このニッケル－マンガン複合水酸化物と水酸化リチウム（ＬｉＯＨ）とを、リチウムとニッケル－マンガンとのモル比がそれぞれ１：１となるようにそれぞれ調製して混合した後、７５０℃の酸素雰囲気で２０時間熱処理して、粒状塊を得た。この後、この粒状塊を粉砕して、組成式$LiNi_{0.50}Mn_{0.50}O_2$（比較例２）で示されるリチウム－ニッケル－マンガン複合酸化物からなる正極活物質を得た。

【００３４】（８）比較例３，４

まず、硫酸ニッケル水溶液のニッケルのモル比と、硫酸マンガン水溶液のマンガンのモル比と、硫酸アルミニウム水溶液のアルミニウムのモル比を９２：３：５および４５：５０：５に調製した２種類の混合水溶液を用意する。ついで、これらの混合水溶液を上述した実施例１～３と同様にして撹拌して、水酸化ニッケルのニッケル元素の一部をマンガン元素およびアルミニウムにより置換された構造を有する、組成式$Ni_{0.92}Mn_{0.03}Al_{0.05}(OH)_2$および$Ni_{0.45}Mn_{0.50}Al_{0.05}(OH)_2$で示される２種類のニッケル－マンガン－アルミニウム複合水酸化物をそれぞれ得た。

【００３５】ついで、リチウムとニッケル－マンガン－アルミニウムとのモル比がそれぞれ１：１となるようにそれぞれ調製して混合した後、上述した実施例１～３と同様にして熱処理および粉砕して、組成式$LiNi_{0.92}Mn_{0.03}Al_{0.05}O_2$（比較例３）および$LiNi_{0.45}Mn_{0.50}Al_{0.05}O_2$（比較例４）で示される２種類のリチウム－ニッケル－マンガン－アルミニウム複合酸化物からなる正極活物質を得た。

【００３６】（９）比較例５

まず、硫酸ニッケル水溶液のニッケルのモル比と、硫酸アルミニウム水溶液のアルミニウムのモル比を９０：１０に調製した混合水溶液を用意する。ついで、これらの混合水溶液を上述した実施例１～３と同様にして撹拌して、水酸化ニッケルのニッケル元素の一部をアルミニウムにより置換された構造を有する、組成式$Ni_{0.90}Al_{0.10}(OH)_2$で示されるニッケル－アルミニウム複合水酸化物をそれぞれ得た。ついで、リチウムとニッケル－アルミニウムとのモル比がそれぞれ１：１となるようにそれぞれ調製して混合した後、上述した実施例１～３と同様にして熱処理および粉砕して、組成式$LiNi_{0.90}Al_{0.10}O_2$（比較例５）で示されるリチウム－ニッケル－アルミニウム複合酸化物からなる正極活物質を得た。

【００３７】（１０）比較例６～７

まず、硫酸ニッケル水溶液のニッケルのモル比と、硫酸マンガン水溶液のマンガンのモル比と、硫酸アルミニウム水溶液のアルミニウムのモル比を８７：３：１０、４５：４５：１０に調製した２種類の混合水溶液を用意する。ついで、これらの混合水溶液を上述した実施例１～３と同様にして撹拌して、水酸化ニッケルのニッケル元素の一部をマンガン元素およびアルミニウム元素により置換された構造を有する、組成式$Ni_{0.87}Mn_{0.03}Al_{0.10}(OH)_2$および$Ni_{0.45}Mn_{0.45}Al_{0.10}(OH)_2$で示される２種類のニッケル－マンガン－アルミニウム複合水酸化物をそれぞれ得た。

【００３８】ついで、リチウムとニッケル－マンガン－アルミニウムとのモル比がそれぞれ１：１となるようにそれぞれ調製して混合した後、上述した実施例１～３と同様にして熱処理および粉砕して、組成式$LiNi_{0.87}Mn_{0.03}Al_{0.10}O_2$（比較例６）および$LiNi_{0.45}Mn_{0.45}Al_{0.10}O_2$（比較例７）で示される２種類のリチウム－ニッケル－マンガン－アルミニウム複合酸化物からなる正極活物質を得た。

【００３９】（１１）比較例８～９

まず、硫酸ニッケル水溶液のニッケルのモル比と、硫酸マンガン水溶液のマンガンのモル比と、硫酸アルミニウム水溶液のアルミニウムのモル比を６７：３：３０、４５：２５：３０に調製した２種類の混合水溶液を用意する。ついで、これらの混合水溶液を上述した実施例１～３と同様にして撹拌して、水酸化ニッケルのニッケル元素の一部をマンガン元素およびアルミニウム元素により置換された構造を有する、組成式$Ni_{0.67}Mn_{0.03}Al_{0.30}(OH)_2$および$Ni_{0.45}Mn_{0.25}Al_{0.30}(OH)_2$で示される２種類のニッケル－マンガン－アルミニウム複合水酸化物をそれぞれ得た。

【００４０】ついで、リチウムとニッケル－マンガン－アルミニウムとのモル比がそれぞれ１：１となるようにそれぞれ調製して混合した後、上述した実施例１～３と同様にして熱処理および粉砕して、組成式$LiNi_{0.67}Mn_{0.03}Al_{0.30}O_2$（比較例８）および$LiNi_{0.45}Mn_{0.25}Al_{0.30}O_2$（比較例９）で示される２種類のリチウム－ニッケル－マンガン－アルミニウム複合酸化物からなる正極活物質を得た。

【００４１】（１２）比較例１０～１１

まず、硫酸ニッケル水溶液のニッケルのモル比と、硫酸マンガン水溶液のマンガンのモル比と、硫酸アルミニウム水溶液のアルミニウムのモル比を５７：３：４０、４５：１５：４０に調製した２種類の混合水溶液を用意する。ついで、これらの混合水溶液を上述した実施例１～３と同様にして撹拌して、水酸化ニッケルのニッケル元素の一部をマンガン元素およびアルミニウム元素により置換された構造を有する、組成式$Ni_{0.57}Mn_{0.03}Al_{0.40}(OH)_2$および$Ni_{0.45}Mn_{0.15}Al_{0.40}(OH)_2$で示される２種類のニッケル－マンガン－アルミニウム複合水酸化物をそれぞれ得た。

【００４２】ついで、リチウムとニッケル－マンガン－アルミニウムとのモル比がそれぞれ１：１となるように

それぞれ調製して混合した後、上述した実施例１～３と同様にして熱処理および粉砕して、組成式$LiNi_{0.57}Mn_{0.03}Al_{0.40}O_2$（比較例１０）および$LiNi_{0.45}Mn_{0.15}Al_{0.40}O_2$（比較例１１）で示される２種類のリチウム－ニッケル－マンガン－アルミニウム複合酸化物からなる正極活物質を得た。

【００４３】（１３）比較例１２～１３

まず、硫酸ニッケル水溶液のニッケルのモル比と、硫酸マンガン水溶液のマンガンのモル比と、硫酸アルミニウム水溶液のアルミニウムのモル比を５２：３：４５、４５：１０：４５に調製した２種類の混合水溶液を用意する。ついで、これらの混合水溶液を上述した実施例１～３と同様にして撹拌して、水酸化ニッケルのニッケル元素の一部をマンガン元素およびアルミニウム元素により置換された構造を有する、組成式$Ni_{0.52}Mn_{0.03}Al_{0.45}(OH)_2$および$Ni_{0.45}Mn_{0.10}Al_{0.45}(OH)_2$で示される２種類のニッケル－マンガン－アルミニウム複合水酸化物をそれぞれ得た。

【００４４】ついで、リチウムとニッケル－マンガン－アルミニウムとのモル比がそれぞれ１：１となるようにそれぞれ調製して混合した後、上述した実施例１～３と同様にして熱処理および粉砕して、組成式$LiNi_{0.52}Mn_{0.03}Al_{0.45}O_2$（比較例１２）および$LiNi_{0.45}Mn_{0.10}Al_{0.45}O_2$（比較例１３）で示される２種類のリチウム－ニッケル－マンガン－アルミニウム複合酸化物からなる正極活物質を得た。

【００４５】（１４）比較例１４～１５

まず、硫酸ニッケル水溶液のニッケルのモル比と、硫酸マンガン水溶液のマンガンのモル比と、硫酸アルミニウム水溶液のアルミニウムのモル比を４７：３：５０、４５：５：５０に調製した２種類の混合水溶液を用意する。ついで、これらの混合水溶液を上述した実施例１～３と同様にして撹拌して、水酸化ニッケルのニッケル元素の一部をマンガン元素およびアルミニウム元素により置換された構造を有する、組成式$Ni_{0.47}Mn_{0.03}Al_{0.50}(OH)_2$および$Ni_{0.45}Mn_{0.05}Al_{0.50}(OH)_2$で示される２種類のニッケル－マンガン－アルミニウム複合水酸化物をそれぞれ得た。

【００４６】ついで、リチウムとニッケル－マンガン－アルミニウムとのモル比がそれぞれ１：１となるようにそれぞれ調製して混合した後、上述した実施例１～３と同様にして熱処理および粉砕して、組成式$LiNi_{0.47}Mn_{0.03}Al_{0.50}O_2$（比較例１４）および$LiNi_{0.45}Mn_{0.05}Al_{0.50}O_2$（比較例１５）で示される２種類のリチウム－ニッケル－マンガン－アルミニウム複合酸化物からなる正極活物質を得た。

【００４７】（１５）比較例１６～２１

水酸化リチウム（$LiOH$）、水酸化ニッケル（$Ni(OH)_2$）、硝酸アルミニウム（$Al(NO_3)_3$）および二酸化マンガン（MnO_2）の各元素Ｌｉ，Ｎｉ，Ｍｎ，Ａｌのモル比がそれぞれ１００：９０：１０：０、１００：７０：３０：０、１００：７０：２０：１０、１００：５０：４０：１０、１００：５０：２０：３０、１００：４０：２０：４０となるように調製した。これらを乳鉢において混合した後、上述した実施例１～３と同様にして熱処理および粉砕して、組成式$LiNi_{0.90}Mn_{0.10}O_2$（比較例１６）、$LiNi_{0.70}Mn_{0.30}O_2$（比較例１７）、$LiNi_{0.70}Mn_{0.20}Al_{0.10}O_2$（比較例１８）、$LiNi_{0.50}Mn_{0.40}Al_{0.10}O_2$（比較例１９）、$LiNi_{0.50}Mn_{0.20}Al_{0.30}O_2$（比較例２０）、$LiNi_{0.40}Mn_{0.20}Al_{0.40}O_2$（比較例２１）で示される２種類のリチウム－ニッケル－マンガン複合酸化物および４種類のリチウム－ニッケル－マンガン－アルミニウム複合酸化物からなる正極活物質を得た。

【００４８】上述のようにして作製した比較例１～比較例２１の各正極活物質を順次粉末Ｘ線回折測定装置内に配置し、Ｘ線源として$Cu-K\alpha$とスリット幅が１μｍのスリットを用いて、各正極活物質に$Cu-K\alpha$を照射角θで照射して$2\theta=18.71\pm0.25°$の範囲に存在するピークの半値幅を測定すると、下記の表２に示すような結果となった。また、$2\theta=18.71\pm0.25°$の範囲に存在するピークの強度I_1を測定するとともに、$2\theta=44.54\pm0.25°$の範囲に存在するピークの強度I_2を測定した後、ピークの強度比I_1/I_2を求めると、下記の表２に示すような結果となった。

【００４９】

【表２】

正極活物質の種類	各元素のモル比				b＋c	半値幅（°）	ピークの強度比
	Ｌｉ	Ｎｉ	Ｍｎ	Ａｌ			
比較例１	1.00	1.00	0.00	0.00	0.00	0.17	1.9
比較例２	1.00	0.50	0.50	0.00	0.50	0.21	1.2
比較例３	1.00	0.92	0.03	0.05	0.08	0.20	1.2
比較例４	1.00	0.45	0.50	0.05	0.55	0.21	1.7
比較例５	1.00	0.90	0.00	0.10	0.10	0.17	1.8
比較例６	1.00	0.87	0.03	0.10	0.13	0.17	1.8
比較例７	1.00	0.45	0.45	0.10	0.55	0.19	1.7
比較例８	1.00	0.67	0.03	0.30	0.33	0.21	1.9
比較例９	1.00	0.45	0.25	0.30	0.55	0.20	1.6
比較例10	1.00	0.57	0.03	0.40	0.43	0.17	1.7
比較例11	1.00	0.45	0.15	0.40	0.55	0.20	1.7
比較例12	1.00	0.52	0.03	0.45	0.48	0.19	1.7
比較例13	1.00	0.45	0.10	0.45	0.55	0.19	1.6
比較例14	1.00	0.47	0.03	0.50	0.53	0.18	1.5
比較例15	1.00	0.45	0.05	0.50	0.55	0.20	1.7
比較例16	1.00	0.90	0.10	0.00	0.10	0.27	1.7
比較例17	1.00	0.70	0.30	0.00	0.30	0.25	1.8
比較例18	1.00	0.70	0.20	0.10	0.30	0.31	1.2
比較例19	1.00	0.50	0.40	0.10	0.50	0.29	1.1
比較例20	1.00	0.50	0.20	0.30	0.50	0.30	1.6
比較例21	1.00	0.40	0.20	0.40	0.60	0.27	1.4

【００５０】なお、上記表２において、各元素のモル比においてＬｉは組成式$Li_aMn_bM_cNi_{1-(b+c)}O_2$におけるａを表し、Ｎｉは１－（ｂ＋ｃ）を表し、Ｍｎはｂを表し、Ａｌ（ＭがＡｌの場合）はｃを表している。上記表２より明らかなように、各比較例１～１５および比較例２１の複合酸化物は、０＜ａ＜１．２、０．０５≦ｂ≦０．４５、０≦ｃ≦０．４５かつ、０．０５≦ｂ＋ｃ≦０．５０、即ち、０．５≦１－（ｂ＋ｃ）≦０．９５の条件のいずれかを満たしていないことが分かる。各比較例１６～２０は、Ｘ線源としてＣｕ－Ｋαを用いた粉末Ｘ線回折測定における２θ＝１８．７１±０．２５°の範囲に存在するピークの半値幅が０．１５°～０．２２°でないことが分かる。

【００５１】2.複合酸化物正極の作製

上述のようにして作製された実施例１～１５の正極活物質および比較例１～２１の正極活物質とを用意し、これらの各正極活物質の粉末９０重量部と、人造黒鉛粉末５重量部と、ポリフッ化ビニリデン５重量部のＮ－メチル－２－ピロリドン（ＮＭＰ）溶液とを混合して各実施例１～１５の正極活物質スラリーおよび各比較例１～２１の正極活物質スラリーを調製する。これらの各正極活物質スラリーを、それぞれアルミニウム箔からなる正極集電体の両面にドクターブレード法により塗布して、正極活物質層を形成した後、１５０℃で２時間真空乾燥して、実施例１～１５の正極および比較例１～２１の正極をそれぞれ作製した。

【００５２】３．負極の作製

リチウムイオンを挿入・脱離し得る負極活物質（例えば、天然黒鉛）９５重量部と、ポリフッ化ビニリデン５重量部のＮ－メチル－２－ピロリドン（ＮＭＰ）溶液とを混合して負極活物質スラリーを調製する。この負極活物質スラリーを銅箔からなる負極集電体の両面にドクターブレード法により塗布して、負極活物質層を形成した後、１５０℃で２時間真空乾燥して負極を作製した。なお、負極活物質としては、リチウムイオンを挿入・脱離し得るカーボン系材料、例えば、グラファイト、カーボンブラック、コークス、ガラス状炭素、炭素繊維、またはこれらの焼成体等が好適である。また、酸化錫、酸化チタン等のリチウムイオンを挿入・脱離し得る酸化物を用いてもよい。

【００５３】４．リチウム二次試験電池の作製

上述のようにして作製した実施例１～１５の正極板および比較例１～２１の正極板にリードを取り付けるとともに、上述のようにして作製された負極板にリードを取り付け、これらの各正・負極板をポリプロピレン製のセパレータを介して渦巻状に巻回して各渦巻状電極体とす

る。

【００５４】これらの各渦巻状電極体をそれぞれの電池外装缶（例えば、ＡＡサイズ）に挿入した後、各リードを正極端子あるいは負極端子に接続する。この外装缶内にエチレンカーボネート（ＥＣ）とジエチルカーボネート（ＤＥＣ）の等容積混合溶媒に電解質塩として１モル／リットルの六フッ化リン酸リチウム（$LiPF_6$）を添加した電解液を注入した後、封口して定格容量５８０ｍＡＨの実施例１～１５の試験電池および比較例１～２１の試験電池を構成する。なお、電池の形状は薄型であっても、角形であっても、円筒型であってもどのような形状でも良いし、そのサイズについても特に制限はない。

【００５５】なお、混合溶媒としては、上述したエチレンカーボネート（ＥＣ）にジエチルカーボネート（ＤＥＣ）を混合したもの以外に、水素イオンを供給する能力のない非プロトン性溶媒を使用し、例えば、ジメチルカーボネート（DMC）、エチルメチルカーボネート（EMC）を混合したものを用いることができる。また、電解質としては、上述した$LiPF_6$以外に、$LiBF_4$、$LiClO_4$、$LiN(SO_2C_2F_5)_2$に代表されるイミド塩等を使用することができる。

【００５６】５．試験

（１）充放電サイクル試験

上述のようにして作製した実施例１～１５の各電池および比較例１～２１の各電池を、室温（２５℃）の雰囲気で２００ｍＡの充電電流で４．２Ｖになるまで定電流充電した後、２００ｍＡの放電電流で２．７５Ｖになるまで定電流放電させるという工程を１サイクルとする充放電サイクル試験を繰り返して行った。このような充放電サイクルを繰り返して、放電容量が初期放電容量の９０％を下回るまでのサイクル数求めた。この結果を下記の表３（実施例１～１５の各電池）及び表４（比較例１～２１の各電池）に示す。

【００５７】（２）負荷特性試験

上述のようにして作製した実施例１～１５の各電池および比較例１～２１の各電池を、室温（２５℃）の雰囲気で２００ｍＡの充電電流で４．２Ｖになるまで定電流充電した後、２００ｍＡの放電電流で２．７５Ｖになるまで定電流放電させ、このときの放電容量（ＡｍＡｈ）を求めた。一方、室温（２５℃）の雰囲気で２００ｍＡの充電電流で４．２Ｖになるまで定電流充電した後、４００ｍＡの放電電流で２．７５Ｖになるまで定電流放電させ、このときの放電容量（ＢｍＡｈ）を求めた。このときの放電容量比Ｂ／Ａを負荷特性として算出すると、下記の表３（実施例１～１５の各電池）及び表４（比較例１～２１の各電池）に示すような結果となった。

【００５８】

【表３】

正極活物質の種類	半値幅 (°)	ピークの強度比	サイクル数 (回)	負荷特性 Ｂ／Ａ
実施例1	0.16	1.8	１２０	０．９０
実施例2	0.20	1.5	１２９	０．９１
実施例3	0.22	1.7	１１９	０．９２
実施例4	0.18	1.3	１７２	０．９６
実施例5	0.20	1.1	１７０	０．９７
実施例6	0.19	1.3	１７９	０．９６
実施例7	0.17	1.5	１７６	０．９８
実施例8	0.18	1.5	１７３	０．９７
実施例9	0.20	1.9	１６９	０．９６
実施例10	0.20	1.7	１７５	０．９７
実施例11	0.17	1.8	１７４	０．９５
実施例12	0.18	1.5	１６８	０．９６
実施例13	0.22	1.7	１８１	０．９７
実施例14	0.21	1.1	１７８	０．９７
実施例15	0.21	1.2	１２５	０．９１

【００５９】

【表４】

正極活物質の種類	半値幅(°)	ピークの強度比	サイクル数(回)	負荷特性B／A
比較例1	0.17	1.9	４３	０．７５
比較例2	0.21	1.2	５３	０．７８
比較例3	0.20	1.2	６７	０．８２
比較例4	0.21	1.7	７１	０．８５
比較例5	0.17	1.8	６９	０．８４
比較例6	0.17	1.8	７５	０．８２
比較例7	0.19	1.7	７９	０．８５
比較例8	0.21	1.9	６７	０．８１
比較例9	0.20	1.6	５８	０．８３
比較例10	0.17	1.7	６０	０．８２
比較例11	0.20	1.7	５９	０．８６
比較例12	0.19	1.7	６２	０．８４
比較例13	0.19	1.6	６７	０．８５
比較例14	0.18	1.5	５９	０．８０
比較例15	0.20	1.7	６０	０．８１
比較例16	0.27	1.7	５２	０．７５
比較例17	0.25	1.8	５４	０．７２
比較例18	0.31	1.2	５７	０．７６
比較例19	0.29	1.1	５２	０．７９
比較例20	0.30	1.6	５１	０．７７
比較例21	0.27	1.4	４９	０．７９

【００６０】上記表３と表４の比較から明らかなように、組成式$Li_aMn_bM_cNi_{1-(b+c)}O_2$で表され、０＜ａ＜１．２、０．０５≦ｂ≦０．４５、０≦ｃ≦０．４５かつ、０．０５≦ｂ＋ｃ≦０．５０、即ち、０．５≦１－（ｂ＋ｃ）≦０．９５の条件のいずれをも満たしているとともに、Ｘ線源としてＣｕ－Ｋαを用いた粉末Ｘ線回折測定における２θ＝１８．７１±０．２５°の範囲に存在するピークの半値幅が０．１５°～０．２２°である各実施例１～１５の複合酸化物は、上記条件のいずれかを満たしていない各比較例１～２１の複合酸化物よりもサイクル特性および負荷特性が優れていることが分かる。

【００６１】これは、Ｌｉ－Ｎｉ複合酸化物のＮｉの一部がＭｎ、あるいはＭｎおよびＡｌによって均一に置換されることにより、結晶構造が強化されたためと考えられる。また、実施例１～３および実施例１５の複合酸化物と、実施例４～１４の複合酸化物を比較すると、実施例４～１４の複合酸化物を用いた方がより優れたサイクル特性および負荷特性を有することが分かる。これは、Ｎｉ、Ｍｎ以外の元素（Ａｌ）を適度に複合化させることにより、Ｎｉ、Ｍｎ、Ａｌの均一性がより高まったためと考えられる。

【００６２】６．添加元素の検討（実施例１６～２５）
上述した例においては、Ｌｉ－Ｎｉ複合酸化物のＮｉの一部をＭｎ、あるいはＭｎおよびＡｌで置換する例について説明したが、Ａｌ以外の元素についても検討した。この場合、複合酸化物を作製するための原料として、硫酸ニッケルと硫酸マンガンと、下記の表５に示す化合物を用いて、上述した実施例における硫酸アルミニウムを用いた場合と同様に作製して、実施例１６～２５の複合酸化物とした。

【００６３】

【表５】

正極活物質の種類	硫酸ニッケル硫酸マンガン以外の原料	複合水酸化物の組成	半値幅 (°)	ピークの強度比	サイクル数(回)	負荷特性 B/A
実施例16	H_3BO_4	$Ni_{0.7}Mn_{0.2}B_{0.2}(OH)_2$	0.20	1.2	159	0.94
実施例17	$FeSO_4$	$Ni_{0.7}Mn_{0.2}Fe_{0.1}(OH)_2$	0.19	1.4	153	0.93
実施例18	$VOSO_4$	$Ni_{0.7}Mn_{0.2}V_{0.1}(OH)_2$	0.17	1.5	151	0.95
実施例19	$CrSO_4$	$Ni_{0.7}Mn_{0.2}Cr_{0.1}(OH)_2$	0.20	1.2	160	0.92
実施例20	$CuSO_4$	$Ni_{0.7}Mn_{0.2}Cu_{0.1}(OH)_2$	0.18	1.1	158	0.93
実施例21	$Ga_2(SO_4)_3$	$Ni_{0.7}Mn_{0.2}Ga_{0.1}(OH)_2$	0.20	1.2	157	0.92
実施例22	$Ca(NO_3)_2$	$Ni_{0.7}Mn_{0.2}Ca_{0.1}(OH)_2$	0.18	1.5	151	0.93
実施例23	$Mg(NO_3)_2$	$Ni_{0.7}Mn_{0.2}Mg_{0.1}(OH)_2$	0.20	1.4	149	0.95
実施例24	$Sr(NO_3)_2$	$Ni_{0.7}Mn_{0.2}Sr_{0.1}(OH)_2$	0.19	1.2	160	0.93
実施例25	$Ti(SO_4)_2$	$Ni_{0.7}Mn_{0.2}Ti_{0.1}(OH)_2$	0.21	1.3	153	0.94

【００６４】ついで、上述のよう作製した実施例１６～２５の各複合酸化物を用いて、上述と同様に各複合酸化物正極を作製し、これらの各複合酸化物正極と、上述と同様な負極と、セパレータと、上述と同様な電解液を用いて定格容量５８０ｍＡＨの実施例１６～２５の各電池を構成した。これらの実施例１６～２５の各電池を上述と同様な充放電サイクル試験および負荷特性試験を行うと、上記表５に示すような結果となった。

【００６５】なお、上記表５より明らかなように、実施例１６～２５の各複合酸化物は、Ｘ線源としてＣｕ－Ｋαを用いた粉末Ｘ線回折測定における２θ＝１８．７１±０．２５°の範囲に存在するピークの半値幅が０．１５°～０．２２°の範囲にあり、また、０＜ａ＜１．２、０．０５≦ｂ≦０．４５、０≦ｃ≦０．４５かつ、０．０５≦ｂ＋ｃ≦０．５０、即ち、０．５≦１－（ｂ＋ｃ）≦０．９５の条件のいづれをも満たしていることが分かる。

【００６６】そして、表４の比較例１～２１の複合酸化物と、上記表５の実施例１６～２５の複合酸化物を比較すると、実施例１６～２５の複合酸化物の方が比較例１～２１の複合酸化物よりサイクル特性および負荷特性の両方とも優れていることが分かる。このことから、Ａｌ以外の元素として、Ｂ，Ｆｅ，Ｖ，Ｃｒ，Ｃｕ，Ｇａ，Ｃａ，Ｍｇ，Ｓｒ，Ｔｉ等の元素から選択して用いても良いことが分かる。ただし、表３の実施例８の複合酸化物と、表５の実施例１６～２５の複合酸化物を比較すると、実施例８の複合酸化物を用いた方がサイクル特性および負荷特性の両方とも優れていることが分かる。このことから、Ａｌの複合化の方が、Ｎｉ，Ｍｎの均一性に対してより効果が高いということができる。

【００６７】７．ピーク比の検討上述した実施例１～１５の複合酸化物および実施例１６～２５の複合酸化物を作製するに際に、酸素雰囲気下で７５０℃で２０時間焼成する熱処理を行ったが、この焼成温度によるピーク比の変化について検討した。

【００６８】（１）実施例２６～２８
実施例８と同様の複合水酸化物と水酸化リチウムの混合物を酸素雰囲気下で８００℃で２０時間焼成する熱処理を行ったものを実施例２６の複合酸化物とし、同様に８５０℃で２０時間焼成する熱処理を行ったものを実施例２７の複合酸化物とし、同様に９００℃で２０時間焼成する熱処理を行ったものを実施例２８の複合酸化物とした。

【００６９】（２）実施例２９～３１
実施例２４と同様の複合水酸化物と水酸化リチウムの混合物を酸素雰囲気下で７７０℃で２０時間焼成する熱処理を行ったものを実施例２９の複合酸化物とし、同様に７９０℃で２０時間焼成する熱処理を行ったものを実施例３０の複合酸化物とし、同様に８１０℃で２０時間焼成する熱処理を行ったものを実施例３１の複合酸化物とした。

【００７０】ついで、上述のよう作製した実施例２６～３１の各複合酸化物を用いて、上述と同様に各複合酸化物正極を作製し、これらの各複合酸化物正極と、上述と同様な負極と、セパレータと、上述と同様な電解液を用いて定格容量５８０ｍＡＨの実施例２６～３１の各電池を構成した。これらの実施例２６～３１の各電池を上述と同様な充放電サイクル試験および負荷特性試験を行うと、下記の表６に示すような結果となった。

【００７１】

【表６】

正極活物質の種類	焼成温度（℃）	半値幅（°）	ピークの強度比	サイクル数（回）	負荷特性B／A
実施例26	８００	０．１８	１．２	１７０	０．９６
実施例27	８５０	０．１９	０．８	１７２	０．９５
実施例28	９００	０．１７	０．５	１５９	０．９２
実施例29	７７０	０．２０	１．０	１５７	０．９３
実施例30	７９０	０．２１	０．８	１６９	０．９２
実施例31	８１０	０．１９	０．７	１４５	０．９０

【００７２】上記表６より、ピークの強度比が０．８以上である実施例８の複合酸化物および実施例２６，２７，２９，３０の複合酸化物と、ピークの強度比が０．８未満である実施例２８，３１の複合酸化物とを比較すると、Ｘ線源としてＣｕ－Ｋαを用いた粉末Ｘ線回折測定における２θ＝１８．７１±０．２５°の範囲に存在するピークの半値幅が０．１５°～０．２２°で０＜ａ＜１．２、０．０５≦ｂ≦０．４５、０≦ｃ≦０．４５かつ、０．０５≦ｂ＋ｃ≦０．５０、即ち、０．５≦１－（ｂ＋ｃ）≦０．９５である複合酸化物であってもサイクル特性および負荷特性が低減することが分かる。これは、ピークの強度比が０．８未満であると、$Li_2Ni_8O_{10}$などの不純物が生成し、これが結晶構造に悪影響を及ぼしたためと考えられる。このことから、ピークの強度比が０．８以上の複合酸化物を用いることが好ましい。

【００７３】以上に述べたように、Ｘ線源としてＣｕ－Ｋαを用いた粉末Ｘ線回折測定における２θ＝１８．７１±０．２５°の範囲に存在するピークの半値幅が０．１５°～０．２２°である組成式$Li_aMn_bM_cNi_{1-(b+c)}O_2$（但し、ＭはＢ，Ａｌ，Ｆｅ，Ｖ，Ｃｒ，Ｃｕ，Ｇａ，Ｃａ，Ｍｇ，Ｓｒ，Ｔｉから選択される１種の元素であり、０＜ａ＜１．２、０．０５≦ｂ≦０．４５、０≦ｃ≦０．４５かつ０．５≦１－（ｂ＋ｃ）≦０．９５）で表されるリチウム－ニッケル－マンガン複合酸化物あるいはリチウム－ニッケル－マンガン－Ｍ複合酸化物は、結晶構造が強化されるため、サイクル特性および負荷特性が向上した正極活物質となる。したがって、この活物質を用いた正極のサイクル特性および負荷特性が向上するとともに、この正極を用いたリチウム二次電池のサイクル特性および負荷特性が向上する。

【００７４】なお、上述した実施の形態においては、まず、共沈工程により、硫酸ニッケルと硫酸マンガン、あるいは硫酸ニッケルと硫酸マンガンと硫酸アルミニウム（なお、硫酸アルミニウムに代えて、Ｂ，Ｆｅ，Ｖ，Ｃｒ，Ｃｕ，Ｇａ，Ｃａ，Ｍｇ，Ｓｒ，Ｔｉを含む化合物を用いてもよい）とからなる混合水溶液を撹拌して、混合水溶液のｐＨを変化させて複合水酸化物を沈殿させる。ついで、この沈殿した複合水酸化物と水酸化リチウムを熱処理して複合酸化物を生成させる例について説明した。しかしながら、これに限ることなく、例えば、ニッケル化合物を溶解させた水溶液とマンガン化合物を溶解させた水溶液との混合水溶液、あるいはニッケル化合物を溶解させた水溶液とマンガン化合物を溶解させた水溶液とＭ化合物（但し、ＭはＢ，Ａｌ，Ｆｅ，Ｖ，Ｃｒ，Ｃｕ，Ｇａ，Ｃａ，Ｍｇ，Ｓｒ，Ｔｉから選択される１種の元素）を溶解させた水溶液との混合水溶液を蒸発乾燥させて、各化合物の極微粒子からなる複合原料を得た後、この複合原料と水酸化リチウムを熱処理して複合酸化物を生成させるようにしてもよい。

フロントページの続き

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POSITIVE ELECTRODE ACTIVE MATERIAL FOR LITHIUM SECONDARY BATTERY AND MANUFACTURING METHOD OF SAME, POSITIVE ELECTRODE FOR LITHIUM SECONDARY BATTERY MADE OF A POSITIVE ELECTRODE ACTIVE MATERIAL AND MANUFACTURING METHOD OF SAME, AND LITHIUM SECONDARY BATTERY MADE OF THE POSITIVE ELECTRODE AND MANUFACTURING METHOD OF SAME

[Richiumu nijiden'chiyoh seikyoku busshitsu oyobi sono seizoh houhoh, kono seikyoku busshitsuo mochiita richiumu nijiden'chiyoh seikyoku oyobi sono seizoh houhoh, kono seikyokuo mochiita richiumu nijiden'chi oyobi sono seizoh houhoh]

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(54) [Title of the Invention]

Positive electrode active material for lithium secondary battery and manufacturing method of same, positive electrode for lithium secondary battery made of the positive electrode active material and manufacturing method of same, and lithium secondary battery made of the positive electrode and manufacturing method of same

(57) [Abstract]

[Purpose] The purpose of the present invention is to produce a positive electrode active material with a reinforced crystal structure of lithium-nickel composite oxide so as to produce a positive electrode for lithium secondary battery and a lithium secondary battery with improved cycle characteristics and load characteristics.

[Means of solution] The positive electrode active material for lithium secondary battery of the present invention is provided with a lithium-nickel-manganese composite oxide or lithium-nickel-manganese-M composite oxide shown in structural formula $Li_aMn_bM_cNi_{1-(b+c)}O_2$

(Wherein, M is at least one element selected from the group consisting of B, Al, Fe, V, Cr, Cu, Ga, Ca, Mg, Sr, and Ti, and at the same time, $0<a<1.2$, $0.05\leq b\leq 0.45$, $0\leq c\leq 0.45$ and $0.5\leq 1-(b+c)\leq 0.95$) and having the half-band width of the peak observed at $2\theta=18.71\pm0.25$ degrees is in the range of 0.15 degrees to 0.22 degrees when a measurement is performed by powder X-ray analysis where the Cu-Kα beam is used as the X-ray source.

[Claim of the invention]

[Claim 1] A positive electrode active material for lithium secondary battery containing a material capable of electrochemically storing and releasing lithium as a positive electrode active material, which positive electrode active material for lithium secondary battery is characterized by the fact that a lithium-nickel-manganese composite oxide or lithium-nickel-manganese-M composite oxide shown in structural formula $Li_aMn_bM_cNi_{1-(b+c)}O_2$ (Wherein, M is at least one element selected from the group consisting of B, Al, Fe, V, Cr, Cu, Ga, Ca, Mg, Sr, and Ti, and at the same time, $0<a<1.2$, $0.05\leq b\leq 0.45$, $0\leq c\leq 0.45$ and $0.5\leq 1-(b+c)\leq 0.95$) and having the half-band width of the peak observed at $2\theta=18.71\pm0.25$ degrees is in the range of 0.15 degrees to 0.22 degrees when measurement is performed by powder X-ray analysis where the Cu-Kα beam is used as the X-ray source.

[Claim 2] A positive electrode active material for lithium secondary battery containing a material capable of electrochemically storing and releasing lithium as a positive electrode active material, which positive electrode active material for lithium secondary battery is characterized by the fact that a lithium-nickel-manganese-M composite oxide shown in structural formula $Li_aMn_bM_cNi_{1-(b+c)}O_2$ (Wherein, M is at least one element selected from the group consisting of B, Al, Fe, V, Cr, Cu, Ga, Ca, Mg, Sr, and Ti, and at the same time, $0<a<1.2$, $0.05\leq b\leq 0.45$, $0.05\leq c\leq 0.40$ and $0.5\leq 1-(b+c)\leq 0.95$) and having the half-band width of the peak observed at $2\theta=18.71\pm0.25$ degrees is in the range of 0.15 degrees to 0.22 degrees when measurement is performed by the powder X-ray analysis where the Cu-Kα beam is used as the X-ray source.

[Claim 3] The positive electrode active material for lithium secondary battery described in

claim 1 or claim 2, in which the M in the aforementioned structural formula is Al.

[Claim 4] The positive electrode active material for lithium secondary battery described in one of claim 1 to claim 3, in which the aforementioned lithium-nickel-manganese composite oxide or lithium-nickel-manganese-M composite oxide having the ratio of the intensity of the peak observed at $2\theta=18.71\pm0.25$ degrees (I1) and the intensity of the peak observed at $2\theta=44.54\pm0.25$ degrees (I2), I1/I2, upon measurement by the aforementioned powder X-ray analysis of at least 0.8 is used selectively.

[Claim 5] A method of manufacturing a positive electrode active material for lithium secondary battery having a material capable of electrochemically storing and releasing lithium as a positive electrode active material, which method of manufacturing a positive electrode active material for lithium secondary batteries is characterized by the fact that a substitution process where a portion of the nickel atoms of the lithium-nickel composite oxide are uniformly replaced with Mn or a portion of the nickel atoms are uniformly replaced with Mn and M (Wherein, M is at least one element selected from the group of B, Al, Fe, V, Cr, Cu, Ga, Ca, Mg, Sr, and Ti) is included, and at the same time, a lithium-nickel-manganese composite oxide or lithium-nickel-manganese-M composite oxide shown in the structural formula $Li_aMn_bM_cNi_{1-(b+c)}O_2$ (Wherein, M is the above-mentioned element, and at the same time, $0<a<1.2$, $0.05\leq b\leq 0.45$, $0.05\leq c\leq 0.45$ and $0.5\leq 1-(b+c)\leq 0.95$) and having the half-band width of the peak observed at $2\theta=18.71\pm0.25$ degrees in the range of 0.15 degrees to 0.22 degrees when a measurement is performed by the powder X-ray analysis where the Cu-Kα beam is used as the X-ray source.

[Claim 6] A method of manufacturing a positive electrode active material for lithium secondary battery having a material capable of electrochemically storing and releasing lithium as a positive electrode active material, which method of manufacturing a positive electrode active material for lithium secondary battery is characterized by the fact that the substitution process where a portion of the nickel atoms of lithium-nickel composite oxide are uniformly replaced with Mn and M (Wherein, M is at least one element selected from the group consisting of B, Al,

Fe, V, Cr, Cu, Ga, Ca, Mg, Sr, and Ti) is included, and at the same time, a lithium-nickel-manganese composite oxide or lithium-nickel-manganese-M composite oxide shown in structural formula $Li_aMn_bM_cNi_{1-(b+c)}O_2$ (Wherein, M is the above-mentioned element, and at the same time, $0<a<1.2$, $0.05\leq b\leq 0.45$, $0.05\leq c\leq 0.40$ and $0.5\leq 1-(b+c)\leq 0.95$) and having the half-band width of the peak observed at $2\theta=18.71\pm 0.25$ degrees in the range of 0.15 degrees to 0.22 degrees when a measurement is performed by the powder X-ray analysis where the Cu-Kα beam is used as the X-ray source.

[Claim 7] The method of manufacturing a positive electrode active material for lithium secondary battery described in claim 5 or claim 6 characterized by the fact that a coprecipitation process in which the pH of the mixed solution of a solution with a dissolved nickel compound and a solution with a dissolved manganese compound or a mixed solution of a dissolved nickel compound, a dissolved manganese compound, and a dissolved M compound (Wherein, M is at least one element selected from the group consisting of B, Al, Fe, V, Cr, Cu, Ga, Ca, Mg, Sr, and Ti) is changed in the aforementioned substitution process so as to precipitate a composite hydroxide, is included.

[Claim 8] The method of manufacturing a positive electrode active material for lithium secondary battery described in claim 5 or claim 6 characterized by the fact that an evaporation drying process, in which evaporation drying is performed for the mixed solution of a solution with a dissolved nickel compound and a solution with a dissolved manganese compound or a mixed solution of a dissolved nickel compound, a dissolved manganese compound and a dissolved M compound (wherein, M is at least one element selected from the group consisting of B, Al, Fe, V, Cr, Cu, Ga, Ca, Mg, Sr, and Ti) in the aforementioned substitution process so as to produce a composite raw material comprising fine particles of each of the aforementioned compounds, is included.

[Claim 9] The method of manufacturing a positive electrode active material for lithium secondary battery described in claim 7 or claim 8, in which a heat-treatment process where a

mixture comprising the aforementioned coprecipitated composite hydroxide or the composite raw material made of the aforementioned dried fine particles and a lithium compound under an oxygen atmosphere to form a composite oxide, and a pulverization process where pulverization is performed for the aforementioned composite oxide to produce a powder are provided after the aforementioned coprecipitation process or before the aforementioned evaporation drying process.

[Claim 10] The manufacturing method of the positive electrode active material for lithium secondary battery described in one of claim 5 to claim 9 in which M in the aforementioned structural formula is Al.

[Claim 11] The method of manufacturing a positive electrode active material for lithium secondary battery described in one of claim 5 to claim 10, in which the aforementioned lithium-nickel-manganese composite oxide or lithium-nickel-manganese-M composite oxide having the ratio of the intensity of the peak observed at $2\theta=18.71\pm0.25$ degrees (I1) and the intensity of the peak observed at $2\theta=44.54\pm0.25$ degrees (I2), I1/I2, upon measuring by the aforementioned powder X-ray analysis of at least 0.8 is produced.

[Claim 12] In a positive electrode for lithium secondary battery containing a positive electrode active material capable of electrochemically storing and releasing lithium, a carbon material, and a binder, a positive electrode for lithium secondary battery characterized by the fact that a lithium-nickel-manganese composite oxide or lithium-nickel-manganese-M composite oxide shown in structural formula $Li_aMn_bM_cNi_{1-(b+c)}O_2$ (Wherein, M is the above-mentioned element, and at the same time, $0<a<1.2$, $0.05\leq b\leq 0.45$, $0.05\leq c\leq 0.45$ and $0.5\leq 1-(b+c)\leq 0.95$) and having the half-band width of the peak observed at $2\theta=18.71\pm0.25$ degrees in the range of 0.15 degrees to 0.22 degrees when measurement is performed by powder X-ray analysis where the Cu-Kα beam is used as the X-ray source, is used as the aforementioned positive electrode active material, and at least a carbon material and a binder are mixed with the above-mentioned positive electrode active material.

[Claim 13] In a positive electrode for lithium secondary battery containing a positive

electrode active material capable of electrochemically storing and releasing lithium, a carbon material and a binder, a positive electrode for lithium secondary battery characterized by the fact that a lithium-nickel-manganese-M composite oxide shown in structural formula $Li_aMn_bM_cNi_{1-(b+c)}O_2$ (Wherein, M is the above-mentioned element, and at the same time, $0<a<1.2$, $0.05\leq b\leq 0.45$, $0.05\leq c\leq 0.45$ and $0.5\leq 1-(b+c)\leq 0.95$) and having the half-band width of the peak observed at $2\theta=18.71\pm 0.25$ degrees in the range of 0.15 degrees to 0.22 degrees when a measurement is performed by powder X-ray analysis where the Cu-Kα beam is used as the X-ray source, is used as the aforementioned positive electrode active material, and at least a carbon material and a binder are mixed with the above-mentioned positive electrode active material.

[Claim 14] The positive electrode for lithium secondary battery described in claim 12 or claim 13 in which the M in the aforementioned structural formula is Al.

[Claim 15] The positive electrode for lithium secondary battery described in one of claim 12 to claim 14, in which the aforementioned lithium-nickel-manganese composite oxide or lithium-nickel-manganese-M composite oxide having the ratio of the intensity of the peak observed at $2\theta=18.71\pm 0.25$ degrees (I1) and the intensity of the peak observed at $2\theta=44.54\pm 0.25$ degrees (I2), I1/I2, upon measuring by the aforementioned powder X-ray analysis of at least 0.8 is used selectively.

[Claim 16] A method of manufacturing a positive electrode for lithium secondary battery consisting of depositing a slurry comprised of at least a positive electrode active material capable of electrochemically storing and releasing lithium, a carbon material and a binder onto a current collector, which method of manufacturing a positive electrode for lithium secondary battery is characterized by the fact that a substitution process where a portion of the nickel atoms of lithium-nickel composite oxide are uniformly replaced with Mn or a portion of the nickel atoms are uniformly replaced with Mn and M (Wherein, M is at least one element selected from the group consisting of B, Al, Fe, V, Cr, Cu, Ga, Ca, Mg, Sr, and Ti) is included so as to produce a lithium-nickel-manganese composite oxide or lithium-nickel-manganese-M composite oxide

shown in structural formula $Li_aMn_bM_cNi_{1-(b+c)}O_2$ (Wherein, M is the above-mentioned element, and at the same time, $0<a<1.2$, $0.05\leq b\leq 0.45$, $0.05\leq c\leq 0.45$ and $0.5\leq 1-(b+c)\leq 0.95$) and having the half-band width of the peak observed at $2\theta=18.71\pm0.25$ degrees in the range of 0.15 degrees to 0.22 degrees when a measurement is performed by the powder X-ray analysis where the Cu-Kα beam is used as the X-ray source and used as a positive electrode active material; then, at least a carbon material and a binder are mixed with the above-mentioned positive electrode active material to form a slurry, and the aforementioned slurry is deposited onto a current collector.

[Claim 17] A manufacturing method of a positive electrode for lithium secondary battery consisting of depositing a slurry comprising at least a positive electrode active material capable of electrochemically storing and releasing lithium, a carbon material, and a binder onto a current collector, which method of manufacturing a positive electrode for lithium secondary battery is characterized by the fact that a substitution process where a portion of the nickel atoms of the lithium-nickel composite oxide are uniformly replaced with Mn and M (Wherein, M is at least one element selected from the group consisting of B, Al, Fe, V, Cr, Cu, Ga, Ca, Mg, Sr, and Ti) is included so as to produce a lithium-nickel-manganese-M composite oxide shown in the structural formula $Li_aMn_bM_cNi_{1-(b+c)}O_2$ (Wherein, M is the above-mentioned element, and at the same time, $0<a<1.2$, $0.05\leq b\leq 0.45$, $0.05\leq c\leq 0.40$ and $0.5\leq 1-(b+c)\leq 0.95$) and having the half-band width of the peak observed at $2\theta=18.71\pm0.25$ degrees in the range of 0.15 degrees to 0.22 degrees when measurement is performed by the powder X-ray analysis where the Cu-Kα beam is used as the X-ray source, and it is used as a positive electrode active material; then, at least a carbon material and a binder are mixed with the above-mentioned positive electrode active material to form a slurry, and the aforementioned slurry is deposited onto a current collector.

[Claim 18] The method of manufacturing positive electrode for lithium secondary battery described in claim 17 or claim 18 characterized by the fact that the coprecipitation process, in which the pH of the mixed solution consisting of a solution with a dissolved nickel compound and a solution with a dissolved manganese compound or a mixed solution of a solution with a

dissolved nickel compound, a solution with a dissolved manganese compound and a solution with a dissolved M compound (Wherein, M is at least one element selected from the group consisting of B, Al, Fe, V, Cr, Cu, Ga, Ca, Mg, Sr, and Ti) is changed in the aforementioned substitution process so as to precipitate a composite hydroxide, is included.

[Claim 19] The method of manufacturing a positive electrode for lithium secondary battery described in claim 17 or claim 18 characterized by the fact that the evaporation drying process, in which evaporation drying is performed for the mixed solution of a solution with a dissolved nickel compound and a solution with a dissolved manganese compound or a mixed solution of a solution with a dissolved nickel compound, a solution with a dissolved manganese compound, and a solution with a dissolved M compound (Wherein, M is at least one element selected from the group consisting of B, Al, Fe, V, Cr, Cu, Ga, Ca, Mg, Sr, and Ti) in the aforementioned substitution process so as to produce a composite raw material comprising fine particles of each of the aforementioned compounds, is included.

[Claim 20] The method of manufacturing the positive electrode for lithium secondary battery described in claim 18 or claim 19, in which a heat-treatment process where a mixture comprising the aforementioned coprecipitated composite hydroxide or the composite raw material made of the aforementioned dried fine particles and a lithium compound under an oxygen atmosphere to form a composite oxide, and a pulverization process where pulverization is performed for the aforementioned composite oxide is performed to produce a powder are provided after the aforementioned coprecipitation process or before the aforementioned evaporation drying process.

[Claim 21] The method of manufacturing the positive electrode for lithium secondary battery described in one of claim 16 to claim 20, in which the M in the aforementioned structural formula is Al.

[Claim 22] The method of manufacturing the positive electrode for lithium secondary battery described in one of claim 16 to claim 22, in which the aforementioned lithium-nickel-manganese composite oxide or lithium-nickel-manganese-M composite oxide having the ratio of the

intensity of the peak observed at $2\theta=18.71\pm0.25$ degrees (I1) and the intensity of the peak observed at $2\theta=44.54\pm0.25$ degrees (I2), I1/I2, upon measuring by the aforementioned powder X-ray analysis of at least 0.8 is formed and used as the aforementioned positive electrode active material.

[Claim 23] In a lithium secondary battery provided with a positive electrode having at least a positive electrode active material capable of electrochemically storing and releasing lithium, a carbon material, and a binder, a negative electrode capable of electrochemically storing and releasing lithium metal, lithium alloy or lithium ion, a separator that isolates the above-mentioned two electrodes and a nonaqueous solution, a lithium secondary battery characterized by the fact that a lithium-nickel-manganese composite oxide or lithium-nickel-manganese-M composite oxide shown in structural formula $Li_aMn_bM_cNi_{1-(b+c)}O_2$ (Wherein, M is the above-mentioned element, and at the same time, $0<a<1.2$, $0.05\leq b\leq 0.45$, $0.05\leq c\leq 0.45$ and $0.5\leq 1-(b+c)\leq 0.95$) and having the half-band width of the peak observed at $2\theta=18.71\pm0.25$ degrees in the range of 0.15 degrees to 0.22 degrees when a measurement is performed by the powder X-ray analysis where the Cu-Kα beam is used as the X-ray source, and it is used as the aforementioned positive electrode active material, and the lithium secondary battery is provided with a positive electrode produced by mixing the above-mentioned positive electrode active material with at least a carbon material and a binder, a negative electrode capable of electrochemically storing and releasing lithium metal, lithium alloy or lithium ion, a separator that isolates the above-mentioned two electrodes and a nonaqueous solution.

[Claim 24] In a lithium secondary battery provided with a positive electrode having at least a positive electrode active material capable of electrochemically storing and releasing lithium, a carbon material, and a binder, a negative electrode capable of electrochemically storing and releasing lithium metal, lithium alloy, or lithium ion, a separator that isolates the above-mentioned two electrodes and a nonaqueous solution, a lithium secondary battery characterized by the fact that a lithium-nickel-manganese-M composite oxide shown in structural formula

$Li_aMn_bM_cNi_{1-(b+c)}O_2$ (Wherein, M is the above-mentioned element, and at the same time, $0<a<1.2$, $0.05\leq b\leq 0.45$, $0.05\leq c\leq 0.40$ and $0.5\leq 1-(b+c)\leq 0.95$) and having the half-band width of the peak observed at $2\theta=18.71\pm 0.25$ degrees in the range of 0.15 degrees to 0.22 degrees when a measurement is performed by the powder X-ray analysis where the Cu-Kα beam is used as the X-ray source, and it is used as the aforementioned positive electrode active material, and the lithium secondary battery is provided with a positive electrode produced by mixing the above-mentioned positive electrode active material with at least a carbon material and a binder, a negative electrode capable of electrochemically storing and releasing lithium metal, lithium alloy, or lithium ion, a separator that isolates the above-mentioned two electrodes and a nonaqueous solution.

[Claim 25] The lithium secondary battery described in claim 23 or claim 24, in which the M in the aforementioned structural formula is Al.

[Claim 26] The method of manufacturing the lithium secondary battery described in one of claim 23 to claim 25, in which the aforementioned lithium-nickel-manganese composite oxide or lithium-nickel-manganese-M composite oxide having the ratio of the intensity of the peak observed at $2\theta=18.71\pm 0.25$ degrees (I1) and the intensity of the peak observed at $2\theta=44.54\pm 0.25$ degrees (I2), I1/I2, upon measuring by the aforementioned powder X-ray analysis of at least 0.8 is formed and used as the aforementioned positive electrode active material.

[Claim 23] In a lithium secondary battery provided with a positive electrode having at least a positive electrode active material capable of electrochemically storing and releasing lithium, a carbon material and a binder, a negative electrode capable of electrochemically storing and releasing lithium metal, lithium alloy or lithium ion, a separator that isolates the above-mentioned two electrodes and a nonaqueous solution, a lithium secondary battery characterized by the fact that a lithium-nickel-manganese composite oxide or lithium-nickel-manganese-M composite oxide shown in structural formula $Li_aMn_bM_cNi_{1-(b+c)}O_2$ (Wherein, M is the above-mentioned element, and at the same time, $0<a<1.2$, $0.05\leq b\leq 0.45$, $0.05\leq c\leq 0.45$ and $0.5\leq 1-$

$(b+c)\leq0.95$) and having the half-band width of the peak observed at $2\theta=18.71\pm0.25$ degrees in the range of 0.15 degrees to 0.22 degrees when measurement is performed by the powder X-ray analysis where the Cu-Kα beam is used as the X-ray source, and it is used as the aforementioned positive electrode active material, and the lithium secondary battery is provided with a positive electrode produced by mixing the above-mentioned positive electrode active material with at least a carbon material and a binder, a negative electrode capable of electrochemically storing and releasing lithium metal, lithium alloy or lithium ion, a separator that isolates the above-mentioned two electrodes and a nonaqueous solution.

[Claim 27] In a manufacturing method of a lithium secondary battery provided with a positive electrode having at least a positive electrode active material capable of electrochemically storing and releasing lithium, a carbon material and a binder, a negative electrode capable of electrochemically storing and releasing lithium metal, lithium alloy, or lithium ion, a separator that isolates the above-mentioned two electrodes and a nonaqueous solution, a method of manufacturing a lithium secondary battery characterized by the fact that the method includes the substitution process where a portion of the nickel atoms of lithium-nickel composite oxide are uniformly replaced with Mn or a portion of the nickel atoms are uniformly replaced with Mn and M (Wherein, M is at least one element selected from the group consisting of B, Al, Fe, V, Cr, Cu, Ga, Ca, Mg, Sr, and Ti) is included so as to produce a lithium-nickel-manganese composite oxide or lithium-nickel-manganese-M composite oxide shown in structural formula $Li_aMn_bM_cNi_{1-(b+c)}O_2$ (Wherein, M is the above-mentioned element, and at the same time, $0<a<1.2$, $0.05\leq b\leq0.45$, $0.05\leq c\leq0.45$ and $0.5\leq1-(b+c)\leq0.95$) and having the half-band width of the peak observed at $2\theta=18.71\pm0.25$ degrees in the range of 0.15 degrees to 0.22 degrees when a measurement is performed by the powder X-ray analysis where Cu-Kα beam is used as the X-ray source and used as the aforementioned positive electrode active material; then, at least a carbon material and a binder are mixed with the above-mentioned positive electrode active material to form a slurry, and the aforementioned slurry is deposited onto a current collector to produce a

positive electrode, and furthermore, the positive electrode produced by the aforementioned positive electrode formation process is superimposed with a negative electrode capable of electrochemically storing and releasing the aforementioned lithium metal, lithium alloy, or lithium ion with the aforementioned separator in between and loaded to a battery tube and a nonaqueous solution is filled inside the aforementioned battery tube.

[Claim 28] A method of manufacturing a lithium secondary battery provided with a positive electrode having at least a positive electrode active material capable of electrochemically storing and releasing lithium, a carbon material, and a binder, a negative electrode capable of electrochemically storing and releasing lithium metal, lithium alloy or lithium ion, a separator that isolates the above-mentioned two electrodes and a nonaqueous solution, which method of manufacturing a lithium secondary battery is characterized by the fact that the method includes a substitution process where a portion of the nickel atoms of lithium-nickel composite oxide are uniformly replaced with Mn and M (Wherein, M is at least one element selected from the group consisting of B, Al, Fe, V, Cr, Cu, Ga, Ca, Mg, Sr, and Ti) is included so as to produce a lithium-nickel-manganese composite oxide or lithium-nickel-manganese-M composite oxide shown in structural formula $Li_aMn_bM_cNi_{1-(b+c)}O_2$ (Wherein, M is the above-mentioned element, and at the same time, $0<a<1.2$, $0.05\leq b\leq 0.45$, $0.05\leq c\leq 0.45$ and $0.5\leq 1-(b+c)\leq 0.95$) and having the half-band width of the peak observed at $2\theta=18.71\pm0.25$ degrees in the range of 0.15 degrees to 0.22 degrees when a measurement is performed by the powder X-ray analysis where the Cu-Kα beam is used as the X-ray source and used as the aforementioned positive electrode active material; then, at least a carbon material and a binder are mixed with the above-mentioned positive electrode active material to form a slurry, and the aforementioned slurry is deposited onto a current collector to produce the aforementioned positive electrode, and furthermore, the positive electrode produced by the aforementioned positive electrode formation process is superimposed with a negative electrode capable of electrochemically storing and releasing the aforementioned lithium metal, lithium alloy, or lithium ion with the aforementioned separator in between and

loaded into a battery tube and a nonaqueous solution is filled inside the aforementioned battery tube.

[Claim 29] The method of manufacturing lithium secondary battery described in claim 27 or claim 28 characterized by the fact that the coprecipitation process, in which the pH of the mixed solution of a solution of a dissolved nickel compound and a solution of a dissolved manganese compound or a mixed solution of a solution of a dissolved nickel compound, a solution of a dissolved manganese compound and a solution of dissolved M compound (Wherein, M is at least one element selected from the group consisting of B, Al, Fe, V, Cr, Cu, Ga, Ca, Mg, Sr, and Ti) is changed in the aforementioned substitution process so as to precipitate a composite hydroxide, is included.

[Claim 30] The method of manufacturing a lithium secondary battery described in claim 27 or claim 28 characterized by the fact that the evaporation drying process, in which evaporation drying is performed for the mixed solution comprising a solution with a dissolved nickel compound and a solution with a dissolved manganese compound or a mixed solution comprising a solution with a dissolved nickel compound, a solution with a dissolved manganese compound, and a solution with a dissolved M compound (Wherein, M is at least one element selected from the group consisting of B, Al, Fe, V, Cr, Cu, Ga, Ca, Mg, Sr, and Ti) in the aforementioned substitution process so as to produce a composite raw material comprising a fine particles of each of the aforementioned compounds, is included.

[Claim 31] The method of manufacturing the lithium secondary battery described in one of claim 27 to claim 30, in which a heat-treatment process where a mixture comprising the aforementioned coprecipitated composite hydroxide or the composite raw material made of the aforementioned dried fine particles and a lithium compound under an oxygen atmosphere to form a composite oxide, and a pulverization process where pulverization is performed for the aforementioned composite oxide to produce a powder are provided after the aforementioned coprecipitation process or before the aforementioned evaporation drying process.

[Claim 32] The method of manufacturing the lithium secondary battery described in one of claim 27 to claim 31, in which the M in the aforementioned structural formula is Al.

[Claim 33] The method of manufacturing the lithium secondary battery described in one of claim 27 to claim 32, in which the aforementioned lithium-nickel-manganese composite oxide or lithium-nickel-manganese-M composite oxide having a ratio of the intensity of the peak observed at $2\theta=18.71\pm0.25$ degrees (I1) and the intensity of the peak observed at $2\theta=44.54\pm0.25$ degrees (I2), I1/I2, upon measurement by the aforementioned powder X-ray analysis of at least 0.8 is formed.

[Detailed description of the invention]

[0001]

[Technical field of the invention] The present invention pertains to a positive electrode active material capable of electrochemically storing and releasing lithium, and the invention further pertains to a positive electrode for lithium secondary battery with an improved cycle characteristics and load characteristics and manufacturing method of same, positive electrode for lithium secondary battery made of the positive electrode active material and manufacturing method of same, and lithium secondary battery made of the positive electrode and manufacturing method of same.

[0002]

[Prior art] In recent years, lithium secondary batteries represented by lithium ion batteries comprising a negative active material that utilizes a carbon material capable of storing and releasing the aforementioned lithium metal, lithium alloy or lithium ion and a positive electrode material a lithium-containing transition metal composite oxide such as lithium-cobalt composite material ($LiCoO_2$), lithium-nickel composite material ($LiNiO_2$) and lithium-manganese composite material ($LiMn_2O_4$) are used as a battery for portable electronics and communication machines such as small video cameras, cell phones and notebook computers since high discharge voltage that matches the 4V class, high energy density and high capacity can be achieved despite

being lightweight and small in size, and a lithium secondary battery that utilizes lithium-cobalt composite oxide ($LiCoO_2$) as the positive electrode material is used in practice.

[0003] However, lithium secondary batteries that utilize a lithium-nickel composite oxide ($LiNiO_2$) as the positive electrode material is not used in practice. As a reason, inadequate cycle characteristics of lithium-nickel composite oxide ($LiNiO_2$) based on disturbance of the crystal structure of the material can be mentioned. In addition, due to brittle crystal structure, the material cannot withstand the sudden storing and releasing of lithium ion at a high charge-discharge rates.

[0004] Thus, a method, in which a portion of the nickel element of the lithium-nickel composite oxide ($LiNiO_2$) is replaced with a different element so as to reinforce the crystal structure and to improve the cycle characteristics is being examined. For example, a method, in which a portion of the nickel element of the lithium-nickel composite oxide ($LiNiO_2$) is substituted with the element cobalt and the element manganese to stabilize the crystal structure, and a manganese compound containing trivalent or higher manganese is used so that formation of an inert Li_2MnO_3 or a rock salt made of NiO is electrochemically controlled is proposed in Japanese Kokai [Unexamined] Patent Application No. Hei 8-37007.

[0005]

[Problems to be solved by the invention] However, the effect achieved by the method proposed in Japanese Kokai [Unexamined] Patent Application No. Hei 8-37007 is still inadequate. In the method proposed in the above-mentioned publication, an improvement in cycle characteristics is observed when a heat-treatment is performed for a lithium compound, nickel compound, cobalt compound, and manganese compound in comparison to the case where a portion of the nickel element is replaced with a cobalt element and manganese element but without forming into a composite, but the effect achieved is still inadequate.

[0006] In this case, distribution of the substituted cobalt element and manganese element is non-uniform, and the reinforcement effect on the crystal structure is inadequate. It is known that in

general, an increase in the half-band width of the peak of the powder X-ray analysis occurs when a dissimilar element is non-uniformly mixed with a given substance, and a non-uniform solid solubility of cobalt element and manganese element is suggested since the half-band width of the peak of the powder X-ray analysis of the lithium-nickel-cobalt-manganese composite oxide produced by the method proposed in the above-mentioned Japanese Kokai [Unexamined] Patent Application No. Hei 8-37007 is higher than the half-band width of the case where an element other than nickel is included.

[0007]

[Means to solve the problem and work of invention] Based on the above-mentioned background, the present invention is to eliminate the above-mentioned existing problems, and the purpose of the present invention is to produce a positive electrode active material with a reinforced crystal structure of lithium-nickel composite oxide so as to produce a positive electrode for lithium secondary battery and a lithium secondary battery with improved cycle characteristics and load characteristics.

[0008] Thus, the positive electrode active material for lithium secondary battery is provided with a lithium-nickel-manganese composite oxide or lithium-nickel-manganese-M composite oxide shown in structural formula $Li_aMn_bM_cNi_{1-(b+c)}O_2$ (Wherein, M is at least one element selected from the group consisting of B, Al, Fe, V, Cr, Cu, Ga, Ca, Mg, Sr, and Ti, and at the same time, $0<a<1.2$, $0.05\leq b\leq 0.45$, $0\leq c\leq 0.45$ and $0.5\leq 1-(b+c)\leq 0.95$) and having the half-band width of the peak observed at $2\theta=18.71\pm 0.25$ degrees in the range of 0.15 degrees to 0.22 degrees when a measurement is performed by the powder X-ray analysis where the Cu-Kα beam is used as the X-ray source.

[0009] Furthermore, the positive electrode active material for lithium secondary battery is provided with a lithium-nickel-manganese-M composite oxide shown in structural formula $Li_aMn_bM_cNi_{1-(b+c)}O_2$ (Wherein, M is at least one element selected from the group consisting of B, Al, Fe, V, Cr, Cu, Ga, Ca, Mg, Sr, and Ti, and at the same time, $0<a<1.2$, $0.05\leq b\leq 0.45$, $0\leq c\leq 0.40$

and $0.5 \leq 1-(b+c) \leq 0.95$) and having the half-band width of the peak observed at $2\theta=18.71\pm0.25$ degrees in the range of 0.15 degrees to 0.22 degrees when a measurement is performed by the powder X-ray analysis where the Cu-Kα beam is used as the X-ray source.

[0010] Reduction in discharge capacity occurs in a lithium-nickel composite oxide shown in $LiNiO_2$ as a result of decomposition of the crystal structure, which is believed to be caused by a brittle crystal structure. However, when a lithium-nickel-manganese composite oxide or lithium-nickel-manganese-M composite oxide, in which a portion of the nickel element in lithium-nickel composite oxide ($LiNiO_2$) is replaced with Mn or Mn and another element M shown in the above-mentioned structural formula (Wherein, M is at least one element selected from the group consisting of B, Al, Fe, V, Cr, Cu, Ga, Ca, Mg, Sr, and Ti) is used, the half-band width of the peak observed at $2\theta=18.71\pm0.25$ degrees is in the range of 0.15 degrees to 0.22 degrees when a measurement is performed by the powder X-ray analysis where the Cu-Kα beam is used as the X-ray source, can be achieved, thus, reinforcement of the crystal structure is possible.

[0011] The half-band width of the peak of the lithium-nickel composite oxide ($LiNiO_2$) observed at $2\theta=18.71\pm0.25$ degrees is in the range of 0.15 degrees to 0.22 degrees when a measurement is performed by the powder X-ray analysis where the Cu-Kα beam is used as the X-ray source, and this suggests that a uniform substitution with a dissimilar element is possible without causing disturbance in the crystal structure. The crystal structure is reinforced in the lithium-nickel-manganese composite oxide or lithium-nickel-manganese-M composite oxide, in which a portion of the nickel element in the lithium-nickel composite oxide ($LiNiO_2$) is uniformly substituted with an Mn or Mn and another element M; as a result, a positive electrode active material with improved cycle characteristics and load characteristics. Thus, the cycle characteristics and load characteristics of the positive electrode made of the above-mentioned active material can be improved, and furthermore, the cycle characteristics and load characteristics of the lithium secondary battery made of the above-mentioned active material can be improved.

[0012] Furthermore, when a lithium-nickel-manganese-Al composite material is used as the

above-mentioned composite oxide, a positive electrode active material with improved cycle characteristics and load characteristics can be produced. Therefore, the cycle characteristics and load characteristics of the positive electrode that utilizes the active material made of the above-mentioned composite oxide are improved and furthermore, the cycle characteristics and load characteristics of the lithium secondary battery that utilizes the above-mentioned positive electrode are improved as well.

[0013] Furthermore, when a lithium-nickel-manganese composite oxide or lithium-nickel-manganese-M composite oxide, in which a portion of the nickel element in the lithium-nickel composite oxide ($LiNiO_2$) is uniformly replaced with Mn or Mn and another element M, and the ratio of the intensity of the peak observed at $2\theta=18.71\pm0.25$ degrees (I1) and the intensity of the peak observed at $2\theta=44.54\pm0.25$ degrees (I2), I1/I2, is below 0.8, formation of impurities such as $Li_2Ni_8O_{10}$ are conceivable. In this case, the impurities have an adverse effect on crystal structure, which leads to problems such as reduction in capacity; thus, it is desirable for the value of the intensity ratio, I1/I2, to be at least 0.8.

[0014] In a conventional synthesis method where mixing is performed for the raw material powders and baking is done is used in production of a lithium-nickel-manganese composite oxide or lithium-nickel-manganese-M composite oxide, in which a portion of the nickel element in the lithium-nickel composite oxide ($LiNiO_2$) is uniformly replaced with Mn or Mn and another element M, it is difficult to uniformly replace a portion of the nickel element in the lithium-nickel composite oxide ($LiNiO_2$) with Mn or Mn and other element M, as a result, the value of the half-band width measured by the powder X-ray analysis is increased, and the degree of improvement in the cycle characteristics and load characteristics is insufficient.

[0015] Therefore, in the method of manufacturing the positive electrode active material of the present invention, uniform replacement of a portion of the nickel element of lithium-nickel composite oxide ($LiNiO_2$) with a lithium-nickel-manganese composite oxide or lithium-nickel-manganese-M composite oxide is required. For example, a coprecipitation process, in which the

pH of a mixed solution consisting of a solution with a dissolved nickel compound and a solution with a dissolved manganese compound or a mixed solution comprising a solution with a dissolved nickel compound, a solution with a dissolved manganese compound and a solution with a dissolved M compound (Wherein, M is at least one element selected from the group consisting of B, Al, Fe, V, Cr, Cu, Ga, Ca, Mg, Sr, and Ti) is changed in the aforementioned substitution process so as to precipitate a composite hydroxide, is required.

[0016] As a different example, an evaporation drying process, in which evaporation drying is performed for the mixed solution consisting of a solution with a dissolved nickel compound and a solution with a dissolved manganese compound or a mixed solution of a solution with a dissolved nickel compound, a solution with a dissolved manganese compound, and a solution with a dissolved M compound (Wherein, M is at least one element selected from the group consisting of B, Al, Fe, V, Cr, Cu, Ga, Ca, Mg, Sr, and Ti) in the aforementioned substitution process so as to produce a composite raw material comprising fine particles of each of the aforementioned compounds, is required. Furthermore, when a heat-treatment is performed for a mixture of the composite hydroxide produced in the above-mentioned process (coprecipitation process, or evaporation drying process) and a mixture of lithium compound under an oxygen atmosphere, a lithium-nickel-manganese composite oxide or lithium-nickel-manganese-M composite oxide, in which a portion of the nickel in the lithium-nickel composite oxide ($LiNiO_2$) is uniformly replaced with Mn or Mn and another element M, can be produced.

[0017] When the above-mentioned coprecipitation process, or evaporation drying process is provided, it is possible to produce a lithium-nickel-manganese composite oxide or lithium-nickel-manganese-M composite oxide, in which a portion of the nickel element in the lithium-nickel composite oxide ($LiNiO_2$) is uniformly replaced with Mn or Mn and another element M (Wherein, M is at least one element selected from the group consisting of B, Al, Fe, V, Cr, Cu, Ga, Ca, Mg, Sr, and Ti). In the above-mentioned lithium-nickel-manganese composite oxide or lithium-nickel-manganese-M composite oxide, the crystal structure is adequately reinforced, and

a positive electrode active material with improved cycle characteristics and load characteristics can be produced. Therefore, the cycle characteristics and load characteristics of the positive electrode that utilize the above-mentioned active material made of the above-mentioned composite oxide are improved and furthermore, the cycle characteristics and load characteristics of the lithium secondary battery that utilizes the above-mentioned positive electrode are improved as well.

[0018]

[Embodiment of the invention] Suitable embodiments of the present invention are explained in detail below.

1. Production of positive electrode active material

First, three different types of mixed solutions adjusted to form the molar ratio of nickel in a nickel sulfate solution and the molar ratio of manganese in manganese sulfate solution of 95:5, 90:30 and 55:45 were prepared. Each of the above-mentioned mixed solutions was poured into a stirring tank and sodium hydroxide solution was slowly added as stirring was performed in the stirring tank and an adjustment was made to the pH of the mixed solutions. As a result of the above-mentioned stirring, three different types of nickel-manganese composite hydroxide given by the composition formulas $LiNi_{0.95}Mn_{0.05}(OH)_2$, $Ni_{0.70}Mn_{0.30}(OH)_2$, $Ni_{0.55}Mn_{0.45}(OH)_2$, in which a portion of the nickel element in the nickel hydroxide was replaced with the element manganese were produced.

[0019] Subsequently, an adjustment was made for the above-mentioned nickel-manganese hydroxides and lithium hydroxide (LiOH) so as to form a molar ratio of the lithium and nickel-manganese of 1:1 and mixing was performed, then, a heat-treatment was performed at a temperature of 750°C for 20 hours under an oxygen atmosphere to produce a powder fragment. Furthermore, pulverization was performed for the above-mentioned powder fragment produced and production of positive electrode active materials made of three different types of lithium-nickel-manganese composite oxides shown in structural formulas $LiNi_{0.95}Mn_{0.05}O_2$ (Working

Example 1), $LiNi_{0.70}Mn_{0.30}O_2$ (Working Example 2), and $LiNi_{0.55}Mn_{0.45}O_2$ (Working Example 3) was performed.

[0020] (2) Working Examples 4 to 6

First, three different types of mixed solutions adjusted to form the molar ratio of nickel in a nickel sulfate solution, the molar ratio of manganese in manganese sulfate solution and the molar ratio of aluminum in aluminum sulfate solution of 90:5:5, 65:30:5 and 50:45:5 were prepared. Subsequently, stirring was performed for the above-mentioned mixed solutions as in the case of the above-mentioned Working Examples 1 to 3 so as to produce three different types of nickel-manganese-aluminum composite hydroxide shown in the structural formulas of $Ni_{0.90}Mn_{0.05}Al_{0.05}(OH)_2$, $Ni_{0.65}Mn_{0.35}Al_{0.05}(OH)_2$, and $Ni_{0.05}Mn_{0.45}Al_{0.05}(OH)_2$ in which a portion of the nickel element in the nickel hydroxide was replaced with the element manganese and the element aluminum.

[0021] Subsequently, an adjustment was made so as to form the molar ratio of the lithium and nickel-manganese-aluminum of 1:1 and mixing was performed; then, a heat-treatment and pulverization were performed as in the case of working examples 1-3 and production of positive electrode active materials made of three different types of lithium-nickel-manganese-aluminum composite oxides shown in composition formulas $LiNi_{0.90}Mn_{0.05}Al_{0.05}O_2$ (Working Example 4), $LiNi_{0.65}Mn_{0.30}Al_{0.05}O_2$ (Working Example 5), and $LiNi_{0.50}Mn_{0.45}Al_{0.05}O_2$ (Working Example 6) was performed.

[0022] (3) Working Examples 7 to 9

First, three different types of mixed solutions adjusted to form the molar ratio of nickel in a nickel sulfate solution, the molar ratio of manganese in manganese sulfate solution and the molar ratio of aluminum in aluminum sulfate solution of 85:5:10, 70:20:10 and 50:40:10 were prepared. Subsequently, stirring was performed for the above-mentioned mixed solutions as in the case of Working Examples 1 to 3 so as to produce three different types of nickel-manganese-aluminum composite hydroxide shown in the composition formulas $Ni_{0.85}Mn_{0.05}Al_{0.10}(OH)_2$,

$Ni_{0.70}Mn_{0.20}Al_{0.10}(OH)_2$, $Ni_{0.50}Mn_{0.40}Al_{0.10}(OH)_2$,in which a portion of the nickel element in the nickel hydroxide was replaced with element manganese and the element aluminum.

[0023] Subsequently, an adjustment was made so as to form the molar ratio of the lithium and nickel-manganese-aluminum to form 1:1 and mixing was performed, then, a heat-treatment and pulverization were performed as in the case of working examples 1-3 and production of positive electrode active materials made of three different types of lithium-nickel-manganese-aluminum composite oxides shown in the composition formulas $LiNi_{0.85}Mn_{0.05}Al_{0.10}O_2$ (Working Example 8 [sic]), $LiNi_{0.70}Mn_{0.20}Al_{0.10}O_2$ (Working Example 9 [sic]), and $LiNi_{0.50}Mn_{0.40}Al_{0.10}O_2$ (Working Example 10 [sic]) was performed.

[0024] (4) Working examples 10 to 12

First, three different types of mixed solutions adjusted to form the molar ratio of nickel in a nickel sulfate solution, the molar ratio of manganese in manganese sulfate solution and the molar ratio of aluminum in aluminum sulfate solution of 65:5:30, 60:10:30 and 50:20:30 were prepared. Subsequently, stirring was performed for the above-mentioned mixed solutions as in the case of the above-mentioned working examples 1 to 3 to as to produce three different types of nickel-manganese-aluminum composite hydroxide shown in the composition formulas $Ni_{0.65}Mn_{0.05}Al_{0.30}(OH)_2$, $Ni_{0.60}Mn_{0.10}Al_{0.30}(OH)_2$, and $Ni_{0.50}Mn_{0.20}Al_{0.30}(OH)_2$ in which a portion of the nickel element in the nickel hydroxide was replaced with the element manganese and the element aluminum.

[0025] Subsequently, an adjustment was made so as to form the molar ratio of the lithium and nickel-manganese-aluminum to form 1:1 and mixing was performed, then, a heat-treatment and pulverization were performed as in the case of working examples 1-3 and production of positive electrode active materials made of three different types of lithium-nickel-manganese-aluminum composite oxides shown in composition formulas $LiNi_{0.65}Mn_{0.05}Al_{0.30}O_2$ (Working Example 10), $LiNi_{0.60}Mn_{0.10}Al_{0.30}O_2$ (Working Example 11), and $LiNi_{0.50}Mn_{0.20}Al_{0.30}O_2$ (Working Example 12) was performed.

[0026] (5) Working examples 13 to 15

First, three different types of mixed solutions adjusted to form the molar ratio of nickel in a nickel sulfate solution, the molar ratio of manganese in manganese sulfate solution and the molar ratio of aluminum in aluminum sulfate solution of 55:5:40, 50:10:40 and 50:5:45 were prepared. Subsequently, stirring was performed for the above-mentioned mixed solutions as in the case of the above-mentioned working examples 1 to 3 to as to produce three different types of nickel-manganese-aluminum composite hydroxide shown in the composition formulas $Ni_{0.55}Mn_{0.05}Al_{0.40}(OH)_2$, $Ni_{0.50}Mn_{0.10}Al_{0.40}(OH)_2$, and $Ni_{0.50}Mn_{0.05}Al_{0.45}(OH)_2$ in which a portion of the nickel element in the nickel hydroxide was replaced with the element manganese and the element aluminum.

[0027] Subsequently, an adjustment was made so as to form the molar ratio of the lithium and nickel-manganese-aluminum to form 1:1 and mixing was performed, then, a heat-treatment and pulverization were performed as in the case of working examples 1-3 and production of positive electrode active materials made of three different types of lithium-nickel-manganese-aluminum composite oxides shown in composition formulas $LiNi_{0.55}Mn_{0.05}Al_{0.40}O_2$ (Working Example 13), $LiNi_{0.50}Mn_{0.10}Al_{0.40}O_2$ (Working Example 14), and $LiNi_{0.50}Mn_{0.05}Al_{0.45}O_2$ (Working Example 15) was performed.

[0028] Each positive electrode active material of Working Example 1 to Working Example 15 produced as described above was arranged for the powder X-ray analyzer and when measurements were made for each positive electrode active material as Cu-Kα X-rays were applied at a radiation angle of theta using the Cu-Kα X-ray source and a slit with a slit width of 1 μm and measurement was performed for the half-band width of the peaks existing in the range of $2\theta=18.71\pm0.25$ degrees, the results shown in Table I below were obtained. Furthermore, when measurements were made of the intensity of the peaks observed at $2\theta=18.71\pm0.25$ degrees (I1) and the intensity of the peaks observed at $2\theta=44.54\pm0.25$ degrees (I2), I1/I2, the results shown in Table I below were obtained.

[0029]

[Table I]

Type of positive electrode active material	Molar ratio of each element				b+c	Half-band width (°)	Intensity ratio of peak
	Li	Ni	Mn	Al			
Work. Ex. 1	1.00	0.95	0.05	0.00	0.05	0.16	1.8
Work. Ex. 2	1.00	0.70	0.30	0.00	0.30	0.20	1.5
Work. Ex. 3	1.00	0.55	0.45	0.00	0.45	0.22	1.7
Work. Ex. 4	1.00	0.90	0.05	0.05	0.10	0.18	1.3
Work. Ex. 5	1.00	0.65	0.30	0.05	0.35	0.20	1.1
Work. Ex. 6	1.00	0.50	0.45	0.05	0.50	0.19	1.3
Work. Ex. 7	1.00	0.85	0.05	0.10	0.15	0.17	1.5
Work. Ex. 8	1.00	0.70	0.20	0.10	0.30	0.18	1.5
Work. Ex. 9	1.00	0.50	0.40	0.10	0.50	0.20	1.9
Work. Ex. 10	1.00	0.65	0.05	0.30	0.35	0.20	1.7
Work. Ex. 11	1.00	0.60	0.10	0.30	0.40	0.17	1.8
Work. Ex. 12	1.00	0.50	0.20	0.30	0.50	0.18	1.5
Work. Ex. 13	1.00	0.55	0.05	0.40	0.45	0.22	1.7
Work. Ex. 14	1.00	0.50	0.10	0.40	0.50	0.21	1.1
Work. Ex. 15	1.00	0.50	0.05	0.45	0.50	0.21	1.2

[0030] In the Table I above, the relative amount of Li is a in the composition formula $Li_aMn_bM_cNi_{1-(b+c)}O_2$, Ni is 1-(b+c), Mn is b, and Al (when M is Al) is c. As is clearly shown in the above-mentioned Table I, the composite oxides of each working example of 1 to 15 where the half-band width of the peak of the lithium-nickel composite oxide ($LiNiO_2$) observed at $2\theta=18.71\pm0.25$ degrees in the range of 0.15 degrees to 0.22 degrees when measurement is done by the powder X-ray analysis where the Cu-Kα beam is used as the X-ray source satisfies all the conditions of $0<a<1.2$, $0.05\leq b\leq 0.45$, $0\leq c\leq 0.45$ and $0.05<b+c<0.50$, that is, $0.5\leq 1-(b+c)\leq 0.95$.

[0031] (6) Comparative Example 1

First, the nickel sulfate solution was poured into a stirring tank, and a sodium hydroxide solution was slowly added to the above-mentioned solution as stirring was being performed and an adjustment was made for the pH of the solution. In this manner, production of nickel hydroxide was achieved. Subsequently, mixing was performed for nickel hydroxide and lithium hydroxide in such a manner that the molar ratio of the lithium and nickel of 1:1 could be achieved, and furthermore, a heat-treatment was performed for 20 hours under an oxygen atmosphere at a temperature of 750°C to produce a powder fragment. Furthermore, pulverization was performed for the above-mentioned powder fragment produced and production of a positive electrode active material shown in composition formula $LiNiO_2$ (Comparative Example 1) was achieved.

[0032] (7) Comparative Example 2

First, a mixed solution, in which the molar ratio of the nickel in a nickel sulfate solution and the molar ratio of the manganese in a manganese sulfate solution were adjusted to 50:50 was prepared. Then, the above-mentioned mixed solution was poured into a stirring tank, and a sodium hydroxide solution was slowly added to the above-mentioned mixed solution as stirring was being performed and an adjustment was made for the pH of the mixed solution. In this manner, production of a nickel-manganese hydroxide, in which a portion of the nickel element in the nickel hydroxide was replaced with the element manganese as shown in the composition formulas $Ni_{0.50}Mn_{0.50}(OH)_2$ was achieved.

[0033] Subsequently, mixing was performed for the above-mentioned nickel-manganese composite oxide and a lithium hydroxide (LiOH) in such a manner that a molar ratio of the lithium and nickel-manganese of 1:1 could be achieved, and furthermore, a heat-treatment was performed for 20 hours under an oxygen atmosphere at a temperature of 750°C to produce a powder fragment. Furthermore, pulverization was performed for the above-mentioned powder fragment produced and production of a positive electrode active material shown in composition formula $LiNi_{0.50}Mn_{0.50}O_2$ (Comparative Example 2) was achieved.

The nickel sulfate solution was poured into a stirring tank, and a sodium hydroxide solution was slowly added to the above-mentioned solution as stirring was being performed and an adjustment was made for the pH of the solution. In this manner, production of nickel hydroxide was performed. Subsequently, mixing was performed for nickel hydroxide and lithium hydroxide in such a manner that the molar ratio of the lithium and nickel of 1:1 could be achieved, and furthermore, a heat-treatment was performed for 20 hours under an oxygen atmosphere at a temperature of 750°C to produce a powder fragment. Furthermore, pulverization was performed for the above-mentioned powder fragment produced and production of a positive electrode active material shown in structural formulas $LiNiO_2$ (comparative example 1) was achieved.

[0034] (8) Comparative examples 3 and 4

First, two different types of mixed solutions were prepared, in which the molar ratio of the nickel in a nickel sulfate solution, the molar ratio of the manganese in a manganese sulfate solution, and the molar ratio of aluminum in an aluminum sulfate solution were adjusted to 92:3:5 and 45:50:5. Then, stirring was performed for the above-mentioned mixed solutions as in the case of the above-mentioned Working Examples 1 to 3 so as to produce two different types of nickel-manganese-aluminum composite hydroxide shown in the composition formulas $Ni_{0.92}Mn_{0.03}Al_{0.05}(OH)_2$ and $Ni_{0.45}Mn_{0.50}Al_{0.05}(OH)_2$ in which a portion of the nickel element in the nickel hydroxide was replaced with the element manganese and the element aluminum.

[0035] Subsequently, mixing was performed for the above-mentioned nickel-manganese-aluminum composite oxide with lithium in such a manner that the molar ratio of the lithium and nickel-manganese-aluminum of 1:1 was achieved, and furthermore, a heat-treatment and pulverization were performed as in the case of Working Examples 1 to 3 so as to produce two different types of positive electrode active materials comprising lithium-nickel-manganese-aluminum composite oxides shown in the composition formulas $LiNi_{0.92}Mn_{0.03}Al_{0.05}O_2$ (Comparative Example 3) and $LiNi_{0.45}Mn_{0.50}Al_{0.05}O_2$ (Comparative Example 4).

[0036] (9) Comparative Example 5

First, a mixed solution, in which the molar ratio of the nickel in a nickel sulfate solution and the molar ratio of the aluminum in an aluminum sulfate solution were adjusted to form 90:10. Then, stirring was performed for the above-mentioned mixed solutions as in the case of Working Examples 1 to 3 so as to produce a nickel-aluminum composite hydroxide shown in the composition formula $Ni_{0.90}Al_{0.10}(OH)_2$, in which a portion of the nickel element in the nickel hydroxide was replaced with the element aluminum. Subsequently, mixing was performed for the above-mentioned nickel-aluminum with lithium in such a manner that a molar ratio of the lithium and nickel-aluminum of 1:1 could be achieved, and furthermore, a heat-treatment and pulverization were performed as in the case of Working Examples 1 to 3 so as to produce a positive electrode active material comprising the lithium-nickel-aluminum composite oxide shown in the composition formula $LiNi_{0.90}Al_{0.10}O_2$ (Comparative example 5).

[0037] (10) Comparative Examples 6 and 7

First, two different types of mixed solutions were prepared, in which the molar ratio of the nickel in a nickel sulfate solution, the molar ratio of the manganese in a manganese sulfate solution, and the molar ratio of aluminum in an aluminum sulfate solution were adjusted to 87:3:10 and 45:45:10. Then, stirring was performed for the above-mentioned mixed solutions as in the case of Working Examples 1 to 3 so as to produce two different types of nickel-manganese-aluminum composite hydroxides shown in the composition formulas $Ni_{0.87}Mn_{0.03}Al_{0.10}(OH)_2$ and $Ni_{0.45}Mn_{0.45}Al_{0.10}(OH)_2$ in which a portion of the nickel element in the nickel hydroxide was substituted with a manganese element and an aluminum element.

[0038] Next, mixing was performed for the above-mentioned nickel-manganese-aluminum composite hydroxides with lithium in such a manner that a molar ratio of the lithium and nickel-manganese-aluminum of 1:1 could be achieved, and furthermore, a heat-treatment and pulverization were performed as in the case of working examples 1 to 3 so as to produce two different types of positive electrode active materials comprised of lithium-nickel-manganese-aluminum composite oxides shown in the composition formulas $LiNi_{0.87}Mn_{0.03}Al_{0.10}O_2$

(Comparative Example 6) and $LiNi_{0.45}Mn_{0.45}Al_{0.10}O_2$ (Comparative Example 7).

[0039] (11) Comparative Examples 8 and 9

First, two different types of mixed solutions were prepared, in which the molar ratio of the nickel in a nickel sulfate solution, the molar ratio of the manganese in a manganese sulfate solution, and the molar ratio of aluminum in an aluminum sulfate solution were adjusted to form 67:3:30 and 45:25:30. Then, stirring was performed for the above-mentioned mixed solutions as in the case of Working Examples 1 to 3 above so as to produce two different types of nickel-manganese-aluminum composite hydroxides shown in the composition formulas of and $Ni_{0.67}Mn_{0.03}Al_{0.30}(OH)_2$ and $Ni_{0.45}Mn_{0.25}Al_{0.30}(OH)_2$, in which a portion of the nickel element in the nickel hydroxide was replaced with the element manganese and the element aluminum.

[0040] Next, mixing was performed for the above-mentioned nickel-manganese-aluminum composite oxide with a lithium in such a manner that the molar ratio of the lithium and nickel-manganese-aluminum of 1:1 could be achieved, and furthermore, a heat-treatment and pulverization were performed as in the case of Working Examples 1 to 3 so as to produce two different types of positive electrode active materials comprised of lithium-nickel-manganese-aluminum composite oxides shown in the composition formulas $LiNi_{0.67}Mn_{0.03}Al_{0.30}O_2$ (Comparative Example 8) and $LiNi_{0.45}Mn_{0.25}Al_{0.30}O_2$ (Comparative Example 9).

[0041] (12) Comparative Examples 10 and 11

First, two different types of mixed solutions were prepared, in which the molar ratio of the nickel in a nickel sulfate solution, the molar ratio of the manganese in a manganese sulfate solution, and the molar ratio of aluminum in an aluminum sulfate solution were adjusted to form 57:3:40 and 45:15:40. Then, stirring was performed for the above-mentioned mixed solutions as in the case of Working Examples 1 to 3 so as to produce two different types of nickel-manganese-aluminum composite hydroxides shown in the composition formulas $Ni_{0.57}Mn_{0.03}Al_{0.40}(OH)_2$ and $Ni_{0.45}Mn_{0.15}Al_{0.40}(OH)_2$ in which a portion of the nickel element in the nickel hydroxide was replaced with the element manganese and the element aluminum.

[0042] Next, mixing was performed for the above-mentioned nickel-manganese-aluminum composite oxide with a lithium in such a manner that the molar ratio of the lithium and nickel-manganese-aluminum of 1:1 could be achieved, and furthermore, a heat-treatment and pulverization were performed as in the case of Working Examples 1 to 3 so as to produce two different types of positive electrode active materials comprising lithium-nickel-manganese-aluminum composite oxides shown in the composition formulas $LiNi_{0.57}Mn_{0.03}Al_{0.40}O_2$ (Comparative Example 10) and $LiNi_{0.45}Mn_{0.15}Al_{0.40}O_2$ (Comparative Example 11).

[0043] (13) Comparative Examples 12 and 13

First, two different types of mixed solutions were prepared, in which the molar ratio of the nickel in a nickel sulfate solution, the molar ratio of the manganese in a manganese sulfate solution, and the molar ratio of aluminum in an aluminum sulfate solution were adjusted to 52:3:45 and 45:10:45. Then, stirring was performed for the above-mentioned mixed solutions as in the case of Working Examples 1 to 3 above so as to produce two different types of nickel-manganese-aluminum composite hydroxide shown in the structural formulas of $Ni_{0.52}Mn_{0.03}Al_{0.45}(OH)_2$ and $Ni_{0.45}Mn_{0.10}Al_{0.45}(OH)_2$ in which a portion of the nickel element in the nickel hydroxide was replaced with the element manganese and the element aluminum.

[0044] Next, mixing was performed for the above-mentioned nickel-manganese-aluminum composite oxide with a lithium in such a manner that the molar ratio of the lithium and nickel-manganese-aluminum of 1:1 could be achieved, and furthermore, a heat-treatment and pulverization were performed as in the case of Working Examples 1 to 3 so as to produce two different types of positive electrode active materials comprising the lithium-nickel-manganese-aluminum composite oxides shown in the composition formulas $LiNi_{0.52}Mn_{0.03}Al_{0.45}O_2$ (Comparative Example 12) and $LiNi_{0.45}Mn_{0.10}Al_{0.45}O_2$ (Comparative Example 13).

[0045] (14) Comparative Examples 14 and 15

First, two different types of mixed solutions were prepared, in which the molar ratio of the nickel in a nickel sulfate solution, the molar ratio of the manganese in a manganese sulfate solution, and

the molar ratio of aluminum in an aluminum sulfate solution were adjusted to 47:3:50 and 45:5:50. Then, stirring was performed for the above-mentioned mixed solutions as in the case of the above-mentioned working examples 1 to 3 to as to produce two different types of nickel-manganese-aluminum composite hydroxide shown in the composition formulas of $Ni_{0.47}Mn_{0.03}Al_{0.50}(OH)_2$ and $Ni_{0.45}Mn_{0.05}Al_{0.50}(OH)_2$ in which a portion of the nickel element in the nickel hydroxide was replaced with the element manganese and the element aluminum.

[0046] Next, mixing was performed for the above-mentioned nickel-manganese-aluminum composite oxide with a lithium in such a manner that the molar ratio of the lithium and nickel-manganese-aluminum of 1:1 could be achieved, and furthermore, a heat-treatment and pulverization were performed as in the case of Working Examples 1 to 3 so as to produce two different types of positive electrode active materials comprising lithium-nickel-manganese-aluminum composite oxides shown in the composition formulas $LiNi_{0.47}Mn_{0.03}Al_{0.50}O_2$ (Comparative Example 14) and $LiNi_{0.45}Mn_{0.05}Al_{0.50}O_2$ (Comparative Example 15).

[0047] (15) Comparative Examples 16 to 21

An adjustment was made in such a manner that the following molar ratios of each of the elements Li, Ni, Mn and Al in lithium hydroxide (LiOH), nickel hydroxide ($Ni(OH)_2$), aluminum nitrate ($Al(NO_3)_3$) and manganese dioxide (MnO_2) to form 100:90:10:0, 100:70:20:0, 100:50:40:10, 100:50:20:30, 100:40:20:40 were produced. After mixing was performed for the above-mentioned materials in a mortar, a heat-treatment and pulverization were performed as in the case Working Examples 1 to 3 above so as to produce two different types of positive electrode active materials comprising lithium-nickel-manganese-composite oxides and four different types of positive electrode active materials comprising lithium-nickel-manganese-aluminum composite oxides shown in the composition formulas $LiNi_{0.90}Mn_{0.10}O_2$ (Comparative example 16), $LiNi_{0.70}Mn_{0.30}O_2$ (Comparative Example 17), $LiNi_{0.70}Mn_{0.20}Al_{0.10}O_2$ (Comparative Example 18), $LiNi_{0.50}Mn_{0.40}Al_{0.10}O_2$ (Comparative Example 19), $LiNi_{0.50}Mn_{0.20}Al_{0.30}O_2$ (Comparative Example 20), and $LiNi_{0.40}Mn_{0.20}Al_{0.40}O_2$ (Comparative Example 21).

[0048] Each positive electrode active material of the above-mentioned Comparative Example 1 to Comparative Example 21 produced as described above was arranged for the powder X-ray analyzer and when a measurement was performed for each positive electrode active material as Cu-Kα rays were applied at a radiation angle of theta using the Cu-Kα X-ray source and a slit with a slit width of 1 μm and measurements were made of the half-band width of the peaks existing in the range of $2\theta=18.71\pm0.25$ degrees, and the results shown in Table II below were obtained. Furthermore, when a measurement was performed for the intensity of the peaks observed at $2\theta=18.71\pm0.25$ degrees (I1) and the intensity of the peaks observed at $2\theta=44.54\pm0.25$ degrees (I2), I1/I2, the results shown in Table II below were obtained.

[0049]

[Table II]

Type of positive electrode active material	Molar ratio of each element				b+c	Half-band width (°)	Intensity ratio of peak
	Li	Ni	Mn	Al			
Comp. Ex. 1	1.00	1.00	0.00	0.00	0.00	0.17	1.9
Comp. Ex. 2	1.00	0.50	0.50	0.00	0.50	0.21	1.2
Comp. Ex. 3	1.00	0.92	0.03	0.05	0.08	0.20	1.2
Comp. Ex. 4	1.00	0.45	0.50	0.05	0.55	0.21	1.7
Comp. Ex. 5	1.00	0.90	0.00	0.10	0.10	0.17	1.8
Comp. Ex. 6	1.00	0.87	0.03	0.10	0.13	0.17	1.8
Comp. Ex. 7	1.00	0.45	0.45	0.10	0.55	0.19	1.7
Comp. Ex. 8	1.00	0.67	0.03	0.30	0.33	0.21	1.9
Comp. Ex. 9	1.00	0.45	0.25	0.30	0.55	0.20	1.6
Comp. Ex. 10	1.00	0.57	0.03	0.40	0.43	0.17	1.7
Comp. Ex. 11	1.00	0.45	0.15	0.40	0.55	0.20	1.7
Comp. Ex. 12	1.00	0.52	0.03	0.45	0.48	0.19	1.7
Comp. Ex. 13	1.00	0.45	0.10	0.45	0.55	0.19	1.6
Comp. Ex. 14	1.00	0.47	0.03	0.50	0.53	0.18	1.5
Comp. Ex. 15	1.00	0.45	0.05	0.50	0.55	0.20	1.7
Comp. Ex. 16	1.00	0.90	0.10	0.00	0.10	0.27	1.7
Comp. Ex. 17	1.00	0.70	0.30	0.00	0.30	0.25	1.8
Comp. Ex. 18	1.00	0.70	0.20	0.10	0.30	0.31	1.2
Comp. Ex. 19	1.00	0.50	0.40	0.10	0.50	0.29	1.1
Comp. Ex. 20	1.00	0.50	0.20	0.30	0.50	0.30	1.6
Comp. Ex. 21	1.00	0.40	0.20	0.40	0.60	0.27	1.4

[0050] In Table II above, Li is a in the structural formula $Li_aMn_bM_cNi_{1-(b+c)}O_2$, Ni is 1-(b+c), Mn is b, and Al (when M is Al) is c. As is clearly shown in Table II above, the composite oxides of

each Comparative Examples 1 through 15 where the half-band width of the peak of the lithium-nickel composite oxide ($LiNiO_2$) observed at $2\theta=18.71\pm0.25$ degrees is not in the range of 0.15 degrees to 0.22 degrees when measurement is performed by the powder X-ray analysis where Cu-Kα beam is used as the X-ray source, in other words, the conditions $0<a<1.2$, $0.05\leq b\leq 0.45$, $0\leq c\leq 0.45$ and $0.05<b+c<0.50$, that is, $0.5\leq 1-(b+c)\leq 0.95$, is not met.

[0051] 2. Production of composite oxide positive electrode

Mixing was performed for 90 parts by weight of each of positive electrode active material produced in the above-mentioned Working Examples 1 to 15 and Comparative Examples 1 to 21, 5 parts by weight of synthetic graphite, and N-methyl-2-pyrrolidone (NMP) solution of 5 parts by weight polyvinylidene fluoride and production was performed for positive electrode active material slurries of Working Examples 1 to 15 and positive electrode active material slurries of Comparative Examples 1 to 21. Each of the above-mentioned positive electrode active material slurries was coated onto the both surfaces of a positive electrode current collector made of an aluminum foil using the doctor blade method to form a positive electrode active material layer; then, vacuum drying was performed for 2 hours at 150°C and production of positive electrode of Working Examples 1 to 15 and positive electrode of Comparative Examples 1 to 21 was achieved.

[0052] 3. Production of negative electrode

Mixing was performed for 95 parts by weight of a negative electrode material capable of achieving intercalation and deintercalation of lithium ion (for example, natural graphite) and an N-methyl-2- pyrrolidone (NMP) solution of 5 parts by weight polyvinylidene fluoride to produce a negative electrode slurry. The resulting negative electrode slurry was coated onto both surfaces of a negative electrode current collector made of copper foil using the doctor blade method to form a negative electrode active material layer, then, vacuum drying was performed for 2 hours at 150°C and production of negative electrode was performed. For the negative electrode active material used in this case, a carbon type material capable of achieving intercalation and

deintercalation of lithium ion, for example, graphite, carbon black, coke, glassy carbon, carbon fiber, and baked materials of the same can be used effectively. Furthermore, an oxide capable of achieving intercalation and deintercalation of lithium ion such as tin oxide or titanium oxide can be used in this case as well.

[0053] 4. Production of lithium secondary battery

The lead is attached to the positive electrode plate produced in the above-mentioned working examples 1 to 15 of the present invention and comparative examples 1 to 21, and the lead is attached to the negative electrode plate produced as described above, and the above-mentioned positive electrode plates and negative electrode plates are wrapped in a coil with a separator in between so as to form a coiled electrode.

[0054] Each of the above-mentioned coiled electrodes is loaded into a battery case (AA size, for example), and the leads are connected to the positive terminal and negative terminal, respectively. Then, an electrolyte solution produced by adding 1 mole/liter of lithium phosphate hexafluoride ($LiPF_6$) to an equal volume mixture solvent of ethylene carbonate (EC) and diethyl carbonate (DEC) was injected to the above-mentioned case, and it was sealed to produce the sample batteries of Working Examples 1 to 15 of the present invention and Comparative Examples 1 to 21 with a rated flow capacity of 580 mAH. In this case, the shape of the above-mentioned batteries is not limited, and flat, square, or cylinder-form may be used.

[0055] In this case, in addition to the above-mentioned mixture of ethylene carbonate (EC) and diethyl carbonate (DEC), a mixture of an aprotic solvent without capacity of feeding a hydrogen ion and dimethyl carbonate (DMC), ethyl methyl carbonate (EMC), etc. may be used as well. Furthermore, in addition to the above-mentioned $LiPF_6$, imide salts represented by $LiBF_4$, $LiClO_4$, $LiN(SO_2C_2F_5)_2$, etc. may be used as electrolytes.

[0056] 5. Test

(1) Charge-discharge cycle test

Each battery produced in the above-mentioned Working Examples 1 to 15 and Comparative

Examples 1 to 21 were charged at room temperature (25°C) under 200 mA at a constant current to form 4.2 V, then, discharged under 200 mA at a constant current to form 2.75 V, and the above-mentioned charge-discharge cycle was repeatedly performed. And the number of cycles until the discharge capacity became 90% or less of the initial discharge capacity was obtained. The results obtained are shown in Table III below (Batteries of Working Examples 1 to 15) and Table IV below (batteries of Comparative Examples 1 to 21).

[0057] (2) Load characteristic test

Each battery produced in the above-mentioned Working Examples 1 to 15 and Comparative Examples 1 to 21 was charged at room temperature (25°C) under 200 mA at a constant current to 4.2 V, then, discharged under 200 mA at a constant current to 2.75 V, and charge capacity (AmAh) was obtained. Meanwhile, charging was performed at room temperature (25°C) under 200 mA at a constant current to 4.2 V, then, discharged under 400 mA at a constant current to 2.75 V, and discharge capacity (BmAh) was obtained. The discharge capacity ratio B/A was calculated as the load characteristic, and the results obtained are shown in Table III below (Batteries of Working Examples 1 to 15) and Table IV below (batteries of Comparative Examples 1 to 21).

[0058]

[Table III]

Type of positive electrode active material	Half-band width (°)	Peak intensity ratio	Number of cycles (number)	Load characteristic B/A
Work. Ex. 1	0.16	1.8	120	0.90
Work. Ex. 2	0.20	1.5	129	0.91
Work. Ex. 3	0.22	1.7	119	0.92
Work. Ex. 4	0.18	1.3	172	0.96
Work. Ex. 5	0.20	1.1	170	0.97
Work. Ex. 6	0.19	1.3	179	0.96
Work. Ex. 7	0.17	1.5	176	0.98
Work. Ex. 8	0.18	1.5	173	0.97
Work. Ex. 9	0.20	1.9	169	0.96
Work. Ex. 10	0.20	1.7	175	0.97
Work. Ex. 11	0.17	1.8	174	0.95
Work. Ex. 12	0.18	1.5	168	0.96
Work. Ex. 13	0.22	1.7	181	0.97
Work. Ex. 14	0.21	1.1	178	0.97
Work. Ex. 15	0.21	1.2	125	0.91

[0059]

[Table IV]

Type of positive electrode active material	Half-band width (°)	Peak intensity ratio	Number of cycles (number)	Load characteristic B/A
Comp. Ex. 1	0.17	1.9	13	0.75
Comp. Ex. 2	0.21	1.2	53	0.78
Comp. Ex. 3	0.20	1.2	67	0.82
Comp. Ex. 4	0.21	1.7	71	0.85
Comp. Ex. 5	0.17	1.8	69	0.84
Comp. Ex. 6	0.17	1.8	75	0.82
Comp. Ex. 7	0.19	1.7	79	0.85
Comp. Ex. 8	0.21	1.9	67	0.81
Comp. Ex. 9	0.20	1.6	58	0.83
Comp. Ex. 10	0.17	1.7	60	0.82
Comp. Ex. 11	0.20	1.7	59	0.86
Comp. Ex. 12	0.19	1.7	62	0.84
Comp. Ex. 13	0.19	1.6	67	0.85
Comp. Ex. 14	0.18	1.5	59	0.80
Comp. Ex. 15	0.20	1.7	60	0.81
Comp. Ex. 16	0.27	1.7	52	0.75
Comp. Ex. 17	0.25	1.8	54	0.72
Comp. Ex. 18	0.31	1.2	57	0.76
Comp. Ex. 19	0.29	1.1	52	0.79
Comp. Ex. 20	0.30	1.6	51	0.77
Comp. Ex. 21	0.27	1.4	49	0.79

[0060] As clearly shown in the results in Table III and Table IV, superior cycle characteristics and load characteristics were achieved in the composite oxides in each of Working Examples 1

to 15 shown in the composition formula $Li_aMn_bM_cNi_{1-(b+c)}O_2$ where the half-band width of the peak of the lithium-nickel composite oxide ($LiNiO_2$) observed at $2\theta=18.71\pm0.25$ degrees in the range of 0.15 degrees to 0.22 degrees when the measurement is made by powder X-ray analysis where the Cu-Kα beam is used as the X-ray source and satisfies all the following conditions: $0<a<1.2$, $0.05\leq b\leq 0.45$, $0\leq c\leq 0.45$ and $0.05<b+c<0.50$, that is, $0.5\leq 1-(b+c)\leq 0.95$, in comparison to composite oxide of Comparative Examples 1 to 21, where one of the above-mentioned conditions is not satisfied.

[0061] In this case, it is hypothesized that good results are achieved as a result of the reinforced crystal structure achieved through uniform replacement of a portion of the Ni in Li-Ni composite oxide with Mn or Mn and Al. Furthermore, when a comparison is made among composite oxides of Working Examples 1 to 3 and Working Example 15 and composite oxide of Working Examples 4 to 14, superior cycle characteristics and load characteristics can be achieved when the composite oxide of Working Examples 4 to 14 is used. In this case, it is hypothesized that the good results are achieved as a result of an increase in uniformity in Ni, Mn and Al based on an approximate degree of formation of composite between Ni and the element other than Mn (Al).

[0062] 6. Examination of element added (Working Examples 16 to 25)

In the above-mentioned examples, the case where a part of the Ni in Li-Ni composite oxide is replaced with Mn or Mn and Al is used, and a further examination was performed with elements other than Al. In this case, nickel sulfate, manganese sulfate and compounds listed in Table V below were used as raw materials in production of composite oxides and production was performed as in the case where aluminum sulfate was used and production of composite oxides of Working Examples 16 to 25 was performed.

[0063]

[Table V]

Type of positive electrode active material	Raw material other than nickel sulfate and manganese sulfate	Composition of composite hydroxide	Half-band with (°)	Peak intensity ratio	Number of cycles (number)	Load character-istic B/A
Work. Ex. 16	H_3BO_4	$Ni_{0.7}Mn_{0.2}B_{0.2}(OH)_2$	0.20	1.2	159	0.94
Work. Ex. 17	$FeSO_4$	$Ni_{0.7}Mn_{0.2}Fe_{0.1}(OH)_2$	0.19	1.4	153	0.93
Work. Ex. 18	$VOSO_4$	$Ni_{0.7}Mn_{0.2}V_{0.1}$*$(OH)_2$	0.17	1.5	151	0.95
Work. Ex. 19	$CrSO_4$	$Ni_{0.7}Mn_{0.2}Cr_{0.1}$*$(OH)_2$	0.20	1.2	160	0.92
Work. Ex. 20	$CuSO_4$	$Ni_{0.7}Mn_{0.2}Cu_{0.1}$*$(OH)_2$	0.18	1.1	158	0.93
Work. Ex. 21	$Ga_2(SO_4)_3$	$Ni_{0.7}Mn_{0.2}Ga_{0.1}(OH)_2$	0.20	1.2	157	0.92
Work. Ex. 22	$Ca(NO_3)_2$	$Ni_{0.7}Mn_{0.2}Ca_{0.1}(OH)_2$	0.18	1.5	151	0.93
Work. Ex. 23	$Mg(NO_3)_2$	$Ni_{0.7}Mn_{0.2}Mg_{0.1}(OH)_2$	0.20	1.4	149	0.95
Work. Ex. 24	$Sr(NO_3)_2$	$Ni_{0.7}Mn_{0.2}Sr_{0.1}(OH)_2$	0.19	1.2	160	0.93
Work. Ex. 25	$Ti(SO_4)_2$	$Ni_{0.7}Mn_{0.2}Ti_{0.1}(OH)_2$	0.21	1.3	153	0.94

* Translator's note: illegible - best guess

[0064] Subsequently, with each of the composite oxides produced in the above-mentioned Working Examples 16 to 25, production of composite oxide positive electrodes was performed, and furthermore, production of batteries of Working Examples 16 to 25 with a rated flow capacity of 580 mAH was performed with the above-mentioned negative electrode and separator as described above. For each battery produced above, the charge-discharge cycle test and load characteristics test were performed as described above, and the results obtained are shown in Table V.

[0065] As shown in the results of the above-mentioned Table V, each of the composite oxide of Working Examples 16 to 25 satisfies the half-band width of the peak of the lithium-nickel composite oxide ($LiNiO_2$) observed at $2\theta=18.71\pm0.25$ degrees in the range of 0.15 degrees to

0.22 degrees when measurement is performed by the powder X-ray analysis where Cu-Kα beam is used as the X-ray source satisfying all the following conditions: $0<a<1.2$, $0.05\leq b\leq 0.45$, $0\leq c\leq 0.45$ and $0.05<b+c<0.50$, that is, $0.5\leq 1-(b+c)\leq 0.95$.

[0066] Furthermore, when a comparison is made among composite oxides of Comparative Examples 1 to 21 shown in Table IV and composite oxides of the above-mentioned Working Examples 16 to 25 shown in Table V, superior cycle characteristics and load characteristics can be achieved when the composite oxide of Working Examples 16 to 25 is used. As shown in the results obtained above, as an element other than Al, elements selected from the group consisting of B, Al, Fe, V, Cr, Cu, Ga, Ca, Mg, Sr, and Ti can be used effectively as well. Furthermore, when a comparison is made among composite oxides of Working Examples 8 and Working Examples 16 to 25, superior cycle characteristics and load characteristics can be achieved when the composite oxide of Working Examples 8 is used. In this case, higher uniformity is achieved with Al in comparison to that of Ni and Mn.

[0067] 7. Examination of peak ratio

In production of the above-mentioned composite oxides of Working Examples 1 to 15 and composite oxides of Working Examples 16 to 25, a heat-treatment was performed for 20 hours in an oxygen atmosphere at a temperature of 750°C, and the change in the peak based on the above-mentioned baking temperature was examined.

[0068] (1) Working Examples 26 to 28

A heat-treatment was performed for a mixture of the composite hydroxide of Working Example 8 and lithium hydroxide for 20 hours under an oxygen atmosphere at a temperature of 800°C (composite oxide of Working Example 26), a heat-treatment was performed for 20 hours under an oxygen atmosphere at a temperature of 850°C (composite oxide of Working Example 27), and a heat-treatment was performed for 20 hours under an oxygen atmosphere at a temperature of 900°C (composite oxide of Working Example 28).

[0069] (2) Working Examples 29 to 31

A heat-treatment was performed for a mixture of the composite hydroxide of Working Example 24 and lithium hydroxide for 20 hours under an oxygen atmosphere at a temperature of 770°C (composite oxide of Working Example 29), a heat-treatment was performed for 20 hours under an oxygen atmosphere at a temperature of 790°C (composite oxide of Working Example 30), and a heat-treatment was performed for 20 hours under an oxygen atmosphere at a temperature of 810°C (composite oxide of Working Example 31).

[0070] Subsequently, with each of the composite oxide produced in the above-mentioned Working Examples 26 to 31, production of composite oxide positive electrode was performed as described above, and furthermore, production of batteries of Working Examples 26 to 31 with a rated flow capacity of 580 mAH was performed with the above-mentioned negative electrode and separator as described above. For each battery produced above, the charge-discharge cycle test and load characteristics test were performed as described above, and the results obtained are shown in Table VI.

[0071]

[Table VI]

Type of positive electrode active material	Baking temperature (°C)	Half-band with (°)	Peak intensity ratio	Number of cycles (number)	Load characteristic B/A
Work. Ex. 26	800	0.18	1.2	170	0.96
Work. Ex. 27	850	0.19	0.8	172	0.95
Work. Ex. 28	900	0.17	0.5	159	0.92
Work. Ex. 29	770	0.20	1.0	157	0.93
Work. Ex. 30	790	0.21	0.8	169	0.92
Work. Ex. 31	810	0.19	0.7	145	0.90

[0072] When comparison is made among composite oxide of Working Example 8 and composite oxides of Working Examples 26, 27, 29 and 30 having the peak intensity ratio of 0.8 or higher and composite oxides of Working Examples 28 and 31 having the peak intensity ratio of 0.8 or below, a reduction in cycle characteristics and load characteristics is observed even among composite oxides having the half-band width of the peak of the lithium-nickel composite oxide ($LiNiO_2$) observed at $2\theta=18.71\pm0.25$ degrees in the range of 0.15 degrees to 0.22 degrees when the measurement is made by powder X-ray analysis where the Cu-Kα beam is used as the X-ray source satisfy all the following conditions: $0<a<1.2$, $0.05\leq b\leq 0.45$, $0\leq c\leq 0.45$ and $0.05<b+c<0.50$, that is, $0.5\leq 1-(b+c)\leq 0.95$. In this case, impurities such as $Li_2Ni_8O_{10}$ are formed when the peak intensity ratio is 0.8 or below and the crystal structure is adversely influenced; thus, it is desirable to use a composite oxide having a value of the intensity ratio of at least 0.8.

[0073] As described above, the crystal structure is reinforced in the lithium-nickel-manganese composite oxide or lithium-nickel-manganese-M composite oxide shown in the structural formula $Li_aMn_bM_cNi_{1-(b+c)}O_2$, (Wherein, M is at least one element selected from the group consisting of B, Al, Fe, V, Cr, Cu, Ga, Ca, Mg, Sr, and Ti, and at the same time, $0<a<1.2$,

$0.05 \leq b \leq 0.45$, $0 \leq c \leq 0.40$ and $0.5 \leq 1-(b+c) \leq 0.95$) and having the half-band width of the peak observed at $2\theta = 18.71 \pm 0.25$ degrees in the range of 0.15 degrees to 0.22 degrees when the measurement is made by powder X-ray analysis where the Cu-Kα beam is used as the X-ray source. Thus, the cycle characteristics and load characteristics of positive electrodes made of the above-mentioned active material can be improved, and furthermore, the cycle characteristics and load characteristics of the lithium secondary batteries made of the above-mentioned active material can be improved.

[0074] In the above-mentioned embodiments, first, the coprecipitation process, in which stirring is performed for a mixed solution of nickel sulfate and manganese sulfate, or nickel sulfate, manganese sulfate and an aluminum sulfate (In this case, instead of an aluminum sulfate, a compound containing B, Al, Fe, V, Cr, Cu, Ga, Ca, Mg, Sr, or Ti may be used, as well) so as to change the pH of the mixed solution and precipitation of the composite hydroxide is performed, then, a heat-treatment is further performed for the above-mentioned composite hydroxide produced and lithium hydroxide to produce the composite oxide. But the present invention is not limited to the above-mentioned embodiments, for example, the evaporation drying process can be used as well, in which evaporation drying is performed for the mixed solution consisting of a solution with a dissolved nickel compound and a solution with a dissolved manganese compound or a mixed solution consisting of a solution with a dissolved nickel compound, a solution with a dissolved manganese compound and a solution with a dissolved M compound (Wherein, M is at least one element selected from the group consisting of B, Al, Fe, V, Cr, Cu, Ga, Ca, Mg, Sr, and Ti) so as to produce a composite raw material comprising fine particles of each of the aforementioned compounds, and a heat-treatment is performed for the above-mentioned composite raw material and lithium hydroxide to produce a composite oxide.